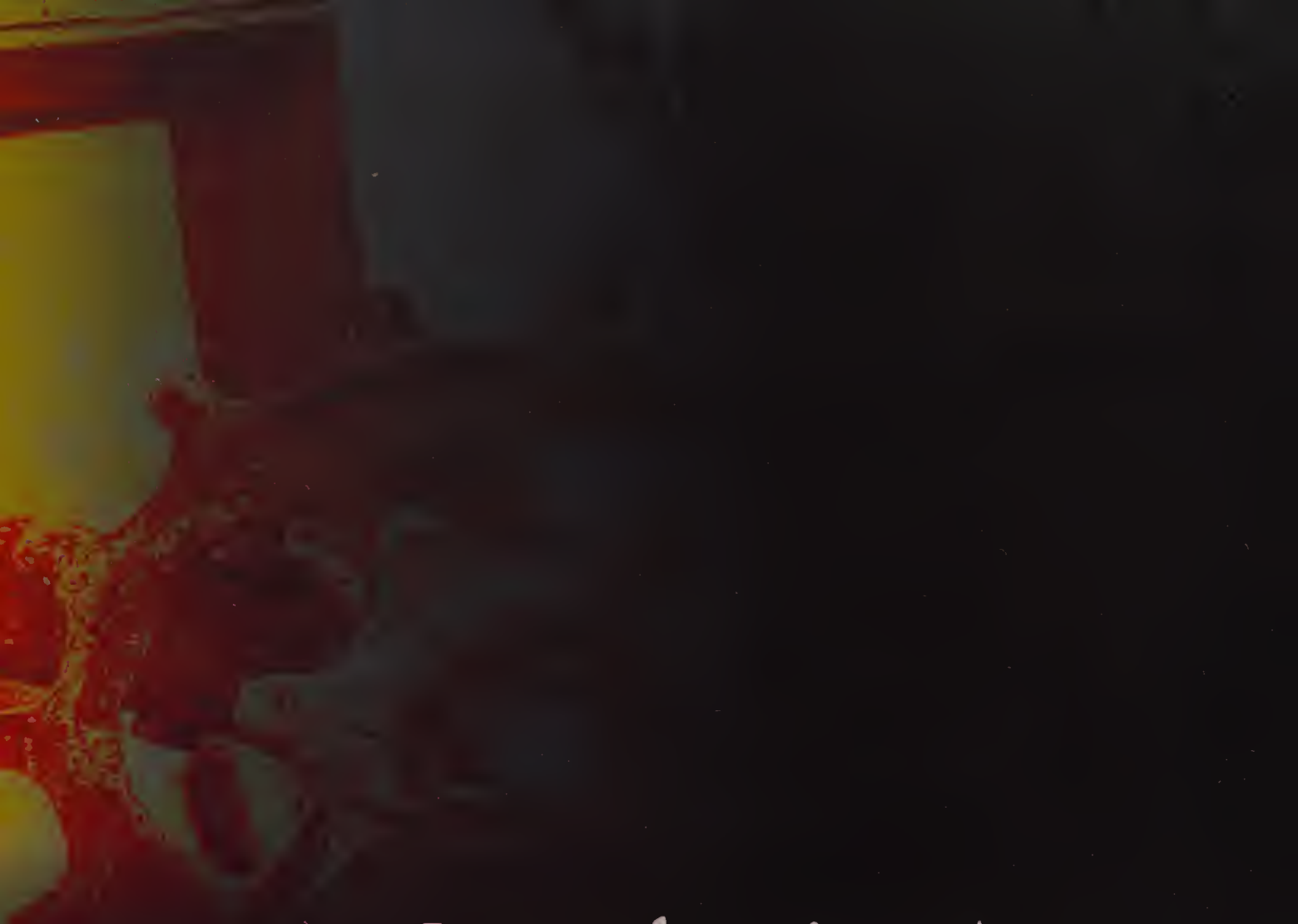

Introduction to Statistical Mechanics

S K Sinha

Alpha Science

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Statistical Mechanics

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S K Sinha

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Alpha Science International Ltd.
Oxford, U.K.

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Alpha Science International Ltd.
7200 The Quorum, Oxford Business Park North
Garsington Road, Oxford OX4 2JZ, U.K.

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Printed from the camera-ready copy provided by the Author.

ISBN 1-84265-302-4

Printed in India

Dedicated to my father

Harihar Prasad Singh

who initiated me into study of mathematics

PREFACE

Statistical mechanics is an indispensable tool for studying the physical properties of matter. Statistical mechanics, together with quantum mechanics, provides the foundation of modern physics which gives a thorough understanding of physical phenomena from the microscopic viewpoint. A basic knowledge of statistical mechanics is, therefore, of vital importance not only for physicist but also for chemists, biologists, metallurgists, material scientists and engineers.

For the last thirty-five years or so, there has been a remarkable growth in our understanding of statistical mechanics. These advances include the theory of the equilibrium state and that of the non-equilibrium state. In the first case, we can deal with the situation from the probability distribution in position, whereas in the second, we need to consider space- and time- dependent correlation functions. Studying non-equilibrium phenomena helps us understand the process through which a physical system, initially in a non-equilibrium state, approaches a state of equilibrium in course of time. Non-equilibrium phenomena, such as fluctuations and transport properties, have wide applications in a variety of fields. Many books have been written on the subject. However, most of them usually do not cover large areas of the equilibrium and non-equilibrium phenomena so important for understanding physical processes. I have tried to give a simple account of them in this book.

This book is thoroughly revised and enlarged version of the lecture notes prepared during the last twenty years for the postgraduate students. This book contains fundamental topics arranged in fifteen chapters. We begin with a brief review of thermodynamic in chapter-1. The next four chapters present the basic theory of equilibrium statistical mechanics. The following three chapters are devoted to its applications to ideal systems. Chapters 9 and 10 present the theory of interacting systems. In chapter 9, the classical system is discussed, whereas Chapter-10 deals with the quantum system. Chapter 11 describes the theory of dense gases and liquids. Chapter-12 is concerned with the statistical mechanics of solids. In chapter-13, phase transition and critical phenomena are considered. The last two chapters are devoted to non-equilibrium statistical mechanics.

The aim of this book is to explain clearly the basic laws of statistical physics and apply them to a wide range of interesting problems. The development of statistical mechanics presented here is self-contained. However, the pre-requisite for a clear understanding of this book is an elementary knowledge of thermodynamics, and classical and quantum mechanics. For more interested readers, an extensive bibliography is provided.

Muzaffarpur, Bihar, India

S. K. SINHA

ACKNOWLEDGEMENTS

The completion of this project has left me indebted to many. It was the pressing demand from many of my students and colleagues for publishing this book. I am indebted to them particularly Dr. Balram Rai, R.D.S. College, Muzaffarpur, Dr. T. K. Dey, L.S.College, Muzaffarpur and S. C. Singh, Patna Collegiate, Patna who took keen interest, while the work was in progress. I express my immense gratitude to Professor Yashwant Singh, Department of Physics, B.H.U., Varanasi, who inspired me to work on this book.

I have consulted many books and journals, some of which are mentioned in the bibliography at the end of the book. I am indebted to those who have written on the subject earlier. I would like to mention, in particular, the work of Pathria, Landau and Lifshitz, Huang and Kubo, which have been my constant reference for several years and which have influenced me to write on the subject.

I would like to express my gratitude to my wife Dr. Kaushalya Sinha, who relieved me of all household duties during the time I worked on this book, I am thankful to Mr. Shiv Pujan Singh, PCS, Muzaffarpur, for neat and clean typing the manuscript. Lastly, I must appreciate very much the keen interest taken by the Narosa Publishing House, New Delhi, particularly for making many useful suggestions for the presentation of this book in the present form.

Muzaffarpur, Bihar

S. K. Sinha

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INTRODUCTION

Statistical mechanics is a scheme for studying the macroscopic properties of systems in terms of their microscopic properties. It is mechanics because it deals with mechanical systems, and statistical because it makes only imprecise (or statistical) predictions. The general character of statistical mechanics does not depend on the mechanics (classical or quantum), which applies only to the idealised situation in which we obtain complete information concerning the motion of a mechanical system.

In principle, we can obtain complete information about a system by constructing and solving its s equations of motion, where s is the number of degrees of freedom. For a system having a very large number of degrees of freedom, the theory of mechanics is, in general, impracticable because the information is incomplete.

Statistical mechanics aims to study the physical properties of a mechanical system in a situation when the description is incomplete. The basic mathematical tool in this approach is the theory of probability. Only statistical or probabilistic consideration can yield a theory which predicts macroscopic properties from an atomic model of the system. It is also important to note that the statistical mechanics is concerned with the relationship between macroscopically measurable parameters (i.e. macroscopic variables), such as volume, pressure, temperature, etc.

Statistical mechanics predicts the average value of the thermodynamic (or macroscopic) properties, which differ from the exact value. However, the deviation from the exact value decreases with the increase in the size of the system (i.e. with the increase in the number of particles in the system). So the statistical predictions are nearly correct for a system consisting of a very large number of particles. Thus, statistical mechanics is an extremely useful tool for solving many-body problems.

It is important to understand the difference between statistical mechanics and thermodynamics, as both deal with common fields. Thermodynamics is based on some basic postulates called the laws of thermodynamics from which all the thermodynamic properties can be deduced. However, thermodynamics gives no information at all regarding the explanation of thermodynamic properties of the system on the basis of a molecular theory. It is statistical mechanics that provides a molecular theory of the thermodynamic properties of a macroscopic system. Thus, statistical mechanics connects mechanics with thermodynamics, or in other words, it bridges the gap between mechanics and thermodynamics.

Statistical mechanics may be divided into two parts: the theory of equilibrium state and the theory of nonequilibrium state. In the first case, we deal with the situation in which probabilities and average values are independent of time. However, in the second case, we need to consider probabilities and average values depending on time. This helps us understand the process through which a physical system, initially in a nonequilibrium state, approaches a state of equilibrium in course of time.

Further, statistical mechanics may be of two types: classical and quantum, depending on the character of the constituent particles, such as atoms and molecules of the system. When the atoms and molecules constituting the system are governed by the laws of classical mechanics, the corresponding statistical mechanics is called classical statistics. On the other hand, if the constituent particles are governed by the quantum laws, the corresponding statistical mechanics is called quantum statistics.

The scope of statistical mechanics is very wide. It is applicable to all phenomena of macroscopic bodies whose behaviour cannot be completely described by the theory of mechanics (classical or quantum), i.e., it is applicable to physics, chemistry, material science, astronomy and even biology. The objective of statistical mechanics is to explain the macroscopic properties of a system on the basis of the dynamical behaviour of its constituent particles.

Statistical mechanics is currently passing through a period of growth and expansion. But its beginnings were modest. With the realization of the atomic theory of matter, physicists began to think of a theory of gases in which macroscopic laws could be related to the microscopic behaviour of atoms. By the middle of the 19^{th} century, the thermodynamics was a well developed branch of physics and the gas laws had been established. Its principles were assumed as a basis of physics by the so-called energeticists.

Kinetic Theory of Dilute Gases

Several notable physicists like Bernoulli, Herapath, Joule, Kronig, Clausius and Maxwell had attempted to give molecular explanations of the macroscopic properties of gases. Their attempts laid the foundation of the kinetic theory of gases, which is an early form of statistical mechanics. It was Bernoulli (1738) who first started real work on the kinetic theory of gases. He established the fact that the pressure of a gas arose from the impact of the particles on the walls of the container and was inversely proportional to the volume of the container if the temperature remained constant (Boyles' law).

The classical kinetic theory was developed to explain the macroscopic phenomena on the basis of atomic models in which atoms move according to the Laws of Newtonian mechanics.

After Bernoulli, no significant work was done for almost a century. In the 19^{th} century, Herapath (1821), Joule(1851), Kronig (1856), Clausius (1857) and Maxwell (1860) took up the subject in rapid succession. Herapath showed that the pressure P of a gas, which is inversely proportional to the volume V at a given temperature, was independent of the shape of the container. Further it was assumed that at a given temperature the speed of the molecules is independent of both pressure and volume. Joule had advanced the kinetic theory by establishing the equivalence of heat and work or motion. Assuming the molecular speed c to be the same for all the molecules, Joule had also shown that the pressure P of a gas is proportional to c^2. Kronig went a step further and derived an expression for pressure

$$P = (1/3)(Nmc^2/V) \tag{I.1}$$

where N is the number of molecules in volume V and m the mass of a molecule. This expression was derived on the assumption that the molecular speed c is the same for all molecules.

Clausius (1857) assumed that the molecules of a gas move with different speeds, and not with the same speed, and modified the ideal-gas equation by replacing c^2 of Eq.(I.1) by $\overline{c^2}$, where $\overline{c^2}$ is the mean square speed of the molecules. Thus Clausius showed that the pressure P of an ideal gas is proportional to the mean square speed $\overline{c^2}$, and not the square of speed, c^2. Clausius, in 1859, also introduced the idea of the mean free path of a molecule between successive collisions. Assuming that all the molecules move with the same speed, Clausius derived an expression for the mean free path:

$$\lambda = 3/4\pi\rho\sigma^2 \tag{I.2}$$

where ρ is the number density of the molecules and σ the molecular diameter. The concept was further used to develop the theory of transport phenomenon, such as diffusion, viscosity and heat conduction. Thus Clausius made a substantial contribution towards the progress of modern kinetic theory. He was hailed as the principal founder of kinetic theory of gases.

The further advances were made by Maxwell and Boltzmann. Maxwell in 1860 formulated the distribution law of velocities of the molecules of a gas. This derivation was based on the probability theory, and should remain invariant under molecular collisions. In a memoir entitled "On the Dynamical Theory of Gases", Maxwell (1867) established what is known as Maxwell's transport equation.

Being attracted perhaps by Maxwell's memoir, Boltzmann entered into the field and made a further significant development in the kinetic theory of gases. In 1872, he derived the famous transport equation in which the physical quantity of interest is the velocity distribution for real gases. Boltzmann was able to show that the transport equation led to equilibrium and that the equilibrium distribution was the generalized Maxwell distribution law, taking into account the presence of external forces. This gave rise to the famous Boltzmann factor $\exp(-\beta U)$, where U denotes the potential energy due to external fields. The generalised distribution is now known as the Maxwell-Boltzmann distribution, applicable to classical systems. Boltzmann also deduced his celebrated H-theorem, where the H-function was identified as the negative of entropy, which provided the molecular interpretation of the law of entropy, and therefore of the irreversibility of macroscopic phenomena.

The so-called energeticists, led by Mach and Ostwald, made heavy attacks on Boltzmann for his H-theorem. They argued that the use of hypothetical concepts such as atoms to describe natural phenomenon was a violation of science's basic function. However, Boltzmann's idea prevailed. Its validity was established by Einstein's theory of Brownian motion, which was verified experimentally by Perrin.

The Boltzmann transport equation is difficult to solve in general. However, after a long gap it was solved by Chapman (1916) and Enskog (1917). Now it has proved to be a powerful tool for investigating the macroscopic properties of systems in non-steady states.

Classical Statistical Mechanics

Most of the early works in kinetic theory were confined to the ideal gases, where the intermolecular potential had been neglected. Although the U of the Boltzmann factor referred originally to the external fields, it was subsequently applied to the treatment of intermolecular interactions of real gases. Clausius (1870) derived the virial theorem. This theorem was used to derive the equation of state for an imperfect gas. Subsequently, J D van der Waals (1873) derived his famous equation of state

$$(P + (a/V^2))\,(V - b) = RT \tag{I.3}$$

on the assumption that the molecules were rigid sphere of diameter σ, and attracted each other with a weak force. It had many successful empirical applications, such as the law of corresponding states and phase transition.

Gibbs followed a somewhat different approach known as the ensemble theory. In this approach, a quantity of central importance is the density distribution function, $\rho(q,p,t)$ of the phase points in the phase space. A stationary distribution ($\partial\rho/\partial t = 0$) characterizes a stationary ensemble, which corresponds to the equilibrium situations. His work was published in the form of a book, "Elementary Principles of Statistical Mechanics" (1902) in which Boltzmann's theory was expounded in the most general and consistent form. However, the book remained unnoticed for a long time. But when the atomic theory of matter became universally recognised, physicists appraised the importance of Gibb's ensemble theory. This is now called Statistical Mechanics.

Deviations from the ideal state were first interpreted qualitatively by the van der Waals equation of state. However, the quantitative interpretation could be given in terms of the virial coefficients, which can be expressed in terms of intermolecular interaction. Ursell (1927) developed a cluster expansion of the partition function. As a result, the partition function of a gas was expressed as a sum

of products of integrals b_l known as cluster integrals. This method was used successfully by Mayer (1937). The cluster expansion method has proven to be exceedingly useful and general for discussing the equilibrium structure and thermodynamic properties of an interacting system. The statistical methods developed in the last three or more decades to explain and predict the equilibrium properties of classical fluids (dense gases and liquids) include Born-Green-Yvon, Percus-Yevick, hypernetted chain and scaled particle methods.

A statistical mechanical perturbation theory, first introduced by Zwanzig (1954) and then improved and generalized by several workers, was proved to be very useful tool to study the equilibrium properties of dense fluids. Statistical ideas began to be applied to liquid crystal and polymer systems with some degree of success. At present, the general framework of classical statistical thermodynamics was well established.

Quantum Statistical Mechanics

The classical statistical mechanics failed to give satisfactory explanation of many physical phenomena, such as blackbody radiation, specific heat of polyatomic gases and solids at low temperatures and the statistical interpretation of entropy. These failures stimulated much theoretical research towards the end of 19^{th} century. Planck (1900) introduced the quantum hypothesis to explain the spectral distribution of the blackbody radiation. The physical importance of this hypothesis as an energy quantization of radiation was recognised several years later by Einstein and Ehrenfest. Einstein (1907) went a step further to combine quantum and statistical ideas to explain the low temperature departure of the specific heats of simple solids from the classical law of Dulong and Petit.

One of the significant failures of classical statistical mechanics was embodied in Gibbs paradox, whereby the entropy of an ideal gas fails to be an additive quantity. This paradox was removed by the quantization of phase space along with a correct counting of identical particles.

This was the framework within which S N Bose began his research on the blackbody radiation. In 1924, Bose derived the Planck's formula on a statistical basis, treating blackbody radiation as a gas of photons (quanta of radiation). This was taken up by Einstein who applied this approach to an ideal gas. Hence it is now called the Bose-Einstein statistics. The new statistics differs from the classical Maxwell-Boltzmann statistics. One of the remarkable achievements of this statistics was its prediction of the famous Bose-Einstein condensation of Bose particles, which was later associated by London (1938) with the so-called λ-transition of liquid He^4 at low temperature.

Pauli (1925) introduced the exclusion principle, according to which no quantum state can accommodate more than one particle. This initiated Fermi(1926) to develop a different kind of statistics, viz the Fermi-Dirac statistics. The relationship between particle statistics and wave function was investigated by Dirac (1926). The Fermi-Dirac statistics was applied to understand the free electrons in metals, dia- and paramagnetism of alkali metals, liquid He^3 near absolute zero. The application of statistical ideas to astrophysical problem was initiated as early as in 1920 by Saha for the case of thermal ionization of plasma. The general problem of plasma was considered by several workers, notably by Vlasov (1938). The Fermi-Dirac statistics was also applied by Fowler, Chanadrashekhar and others to understand the astrophysical problems like white dwarf stars and neutron stars.

In the limit when Planck's constant $h \rightarrow 0$, both the quantum statistics (Bose-Einstein and Fermi-Dirac) reduce to the classical Maxwell-Boltzmann statistics. It is important to mention that the statistics governing a system is connected with the spin of its particles (pauli 1940). Particles having an integral spin (in units of $\hbar$) obey Bose-Einstein statistics, while particles having a half odd integral spin obey Fermi-Dirac statistics.

The best approach to the theory of quantum fluids is given by the density matrix theory, introduced into quantum mechanics by von Neumann (1927) and Dirac (1935). Density matrix is

introduced in the statistical and quantum mechanics in two different ways. In the statistical point of view, a state of quantum ensemble is described by a density operator (or statistical operator) $\hat{\rho}$ the corresponding matrix is called a density matrix. Thus the density matrix is the quantum mechanical analogue of the density function of the classical phase space. The cluster expansion of Kahn and Uhlenbeck (1938) and its elaboration by Lee and Yang (1959, I960) is perhaps the most natural method for the treatment of quantum statistical mechanics. The basic approach in this theory is the same as the one that obtains the cluster expansion for a classical fluid. However, because of the interplay of the quantum statistical effect, and the effect arising from the interparticle interactions, the mathematical structure of the quantum statistical mechanics is considerably involved.

The l-body problem in quantum mechanics can, in principle, be found from the solution of the quantum-mechanical l-body problem. Unfortunately, the actual calculation is too involved to be feasible. It is only the two-body problem in quantum mechanics, which was solved exactly using phase-shift analysis by Beth and Uhlenbeck (1936, 1937).

Another interesting method is the Feyman path integral approach (Feynman and Hibbs 1965). In this approach one begins with the quantum mechanical partition function in which the canonical partition function is represented by a Boltzmaann weighted sum over continuous paths in configurational space. Equilibrium properties of the quantum system can be obtained by solving the equivalent classical problem by using the path integral simulation technique. The path integral methods have been used to study the interesting and difficult problems of quantum systems.

Phase Transitions

The field of phase transitions is an area of current interest. As early as in 1973, van der Waals established the continuity of the gaseous and liquid state and was able to explain the qualitative features of the gas liquid transition, including the existence of a critical point . The van der Waals theory is a typical example of mean field theory. A great step forward was taken by Mayer in 1937, who predicted some features of liquid gas transition. However, the Mayer theory fell short of an explanation of the full condensation phenomena. A decisive theoretical progress towards a better understanding of critical phenomena has come only in recent years. The scaling laws proposed by Widon (1965) and kadanoff (I966) and the renormalizing theory of Wilson (1971) have made much progress in this field. Other area of phase change is the Ising model, originally advanced by Ising in 1925 to study the magnetic ordering. It is a problem in statistical mechanics with spins, arranged in lattice sites. In I944, Onsager solved the two dimensional problem of Ising, showing the logarithmic peak in the specific heat at the transition. In spite of considerable efforts by many workers, the three dimensional model has not been solved fully as yet. Even today, the field of critical point phenomena continues to be an active area of statistical mechanics. Many other aspects of phase transitions are also not fully understood as regard their precise statistical considerations.

Non-Equilibrium Phenomena

To understand irreversible processes fundamental are fluctuation phenomena, of which the prototype is brownian motion of fine particles, discovered by the botanist Robert Brown in 1927. It was clearly explained by Einstein and Smoluchowski (1906) as the result of molecular collision. Perrin in 1908 experimentally verified the theoretical prediction on Brownian motion and also measured the variation of concentration with height for Brownian particles in suspension, thereby providing a signal triumph for the molecular kinetic theory. The studies of fluctuations have proved to be very useful in understanding the dynamics of the systems. The next major investigation were the Schottky effect (1918), in which random thermionic emission in a vacuum tube produces circuit noise on amplification, and Johnson noise (1928), in which circuit noise is generated by the thermal fluctuations in a conductor. The Jonson noise was theoretically analyzed by Nyguist (1928).

The relationship between the fluctuations and the corresponding dissipative process was provided by the fluctuation-dissipation theorem derived originally by Callen and Welton in 1951.

The important advance in the theory was made by Boltzmann, who derived the Boltzmann transport equation. Boltzmann's equation gives a microscopic description of non equilibrium process in the dilute gas and of the approach of the gas to an equilibrium state. Using the Boltzmann equation, Chapman and Enskog derived expressions for the transport coefficient for a dilute gas. The kinetic theory of dense gases began with the work of Enskog, who in 1922 generalized the Boltzmann's derivation of the transport equation to apply it to a dense gas of hard spheres. At the same time, the time correlation function method was developed, which provides expressions for transport coefficients for a wide class of fluid systems, including dilute or dense gases as well as simple liquids. The principal advantage of the time correlation function method is that it provides a new set of microscopic functions for a fluid, which can be studied directly by experiments or by computer simulation methods. Even more than hundred years after the pioneer work of Boltzmann, in 1872, the field of the transport properties continues to be an active area of statistical mechanics.

At present statistical mechanics is being applied in many directions. We have presented here a brief historical development. However, there are many other significant developments which are not included here.

CHAPTER 1

REVIEW OF THERMODYNAMICS

1.1. Introduction

In this chapter we present a brief review of equilibrium thermodynamics. The thermodynamics is based on some basic postulates called the "Laws of thermodynamics" from which all the thermodynamic properties can be deduced. The matter presented here will establish a connection between thermodynamics and statistical mechanics.

In thermodynamics, a system is a definite quantity of matter bounded by some closed surface. A thermodynamic system may consist of a large number of material particles (e.g. molecules, atoms, etc.) or of field quantities such as electromagnetic radiation. The matter and space external to a system is called its surrounding (or environment). A system and its surrounding taken together is called the universe. Thus the system is a part of the universe. The thermodynamic state of a system can be represented by specifying its pressure P, volume V and temperature T. These parameters (P, V, T) provide a macroscopic description of the system and known as thermodynamic parameters or variables. If the thermodynamic variables are independent of time, the system is said to be in a steady state, i.e. the system is in equilibrium.

These thermodynamic variables are connected by the functional relationship

$$F(P, V, T) = 0 \tag{1.1.1}$$

It is generally known as equation of state. Thus the state variables are not all independent and are connected by 'equation of state'. The role of statistical mechanics is the derivation, from the molecular theory, of such equation of state. For example, the equation of state of a gas is

$$PV - nRT = 0 \tag{1.1.2}$$

where n is the number of moles in the system and R is the gas constant for one mole. Eq.(1.1.2) is not accurate for real gases, except in the limit of very low pressure.

Before going to discuss, we pause to introduce some terminology. A thermodynamic process is a change in the state variable of the system. An adiabatic process is one in which no exchange of heat takes place between the system and its surrounding. When a process takes place in such a way that its temperature remains constant, then the process is said to be isothermal. A process is isobaric if the pressure is fixed, isochoric if the density is constant, and quasistatic if the process is infinitely slow. A process is reversible if it can be reversed in each step by infinitesimal changes of the conditions of surrounding. Thus a reversible process is quasistaic in nature and follows a path which can be exactly reversed. A process, which is not reversible, is called irreversible.

Thermodynamics is an empirical science based on four postulates known as laws of thermodynamics namely

(i) Zeroth law of thermodynamics: which provides the thermodynamic definition of temperature.

(ii) First law of thermodynamics: which is the law of conservation of energy, applied to thermodynamic system.

(iii) Second law of thermodynamics: which determines the direction of evolution of thermodynamic process.

(iv) Third law of thermodynamics: which imposes constraints on the process.

From these laws all the equilibrium properties of systems may be deduced logically.

1.2. First Law of Thermodynamics

Let a system changes from an initial state A to a final state B. In this process, let the system absorb an amount of heat ΔQ and perform an amount of work ΔW, then according to the first law of thermodynamics

$$\Delta U = \Delta Q - \Delta W \tag{1.2.1}$$

where ΔU is the change in internal energy of the system and given by

$$\Delta U = U_B - U_A \tag{1.2.2}$$

U_A and U_B are the internal energy of the systems in the states A and B, respectively.

The internal energy is a function of state of the system only. It may be regarded as partly kinetic energy arising from the motion of the particle and partly potential energy arising from the attraction among the particles of the system.

When the charge is infinitesimally small, Eq.(1.2.1) can be written as

$$dU = dQ - \Delta W \tag{1.2.3}$$

This is mathematical form of the first law of thermodynamics.

The first law may be stated in a more elaborate form as:

"When a system changes from an initial state A to a final state B, the increase in internal energy ΔU of the system is the algebraic sum of the work ΔW, the heat ΔQ and mass action quantity ΔZ, which it receives from its surrounding". Thus

$$\Delta U = \Delta W + \Delta Q + \Delta Z \tag{1.2.4}$$

Let us consider an infinitesimal process in which the change in volume is dV at the pressure P, then the work done is given by

$$dW = PdV$$

then substituting this value in Eq.(1.2.3) the first law of thermodynamics is expressed in the form

$$dU = dQ - PdV \tag{1.2.5}$$

Here ΔZ is absent.

In a quasi-static infinitesimal process, the work done is given by

$$dW = -PdV + \sum_i F_i da_i \tag{1.2.6}$$

where F_i is the generalized force and a_i the generalized coordinate of the system.

If dN_i be the change in number of molecules of the i^{th} component of the system due to surrounding and μ_i the chemical potential per molecule of the i^{th} component of the system, then

$$\Delta Z = \sum_i \mu_i dN_i \tag{1.2.7}$$

Substituting these values in (1.2.4), we get

$$dU = dQ - PdV + \sum_i F_i da_i + \sum_i \mu_i dN_i \tag{1.2.8}$$

The first law of thermodynamics simply states that heat and work are mutually convertible in carrying out a process. However, it does not specify the direction of the process under consideration. It has been assumed that every change of thermodynamic state can take place in any direction. Every one knows from experiments that the interchange of heat and work differs in a fundamental way. There exists some directional law in this case, which imposes a limitation on transformation of energy. This is the second law of thermodynamics.

1.3. Second Law of Thermodynamics

The second law of thermodynamics is concerned with the method of transformation of heat into mechanical work and the direction on which the natural process involving energy change occur.

Carnot, while explaining the heat engine, established that it is impossible to convert heat completely into work. Further we see that even for the partial conversion of heat into work, heat must be extracted from a hot body and the portion of heat not converted into work must be given up to a cold body, so that the flow of heat is governed by the temperatures, irrespective of the nature of the working substance. This principle is generally known as the second law of thermodynamics.

The second law is an empirical law. It has been stated in many ways, which are, of course, all equivalent. We express two equivalent statements of the second law in the following forms.

(i) Kelvin statement: "It is impossible to convert all heat taken form a body of uniform temperature into work without causing other changes".

(ii) Claussius statement: "It is impossible for a self acting machine, unaided by any external agency, to transfer heat from a cold body to a hot body".

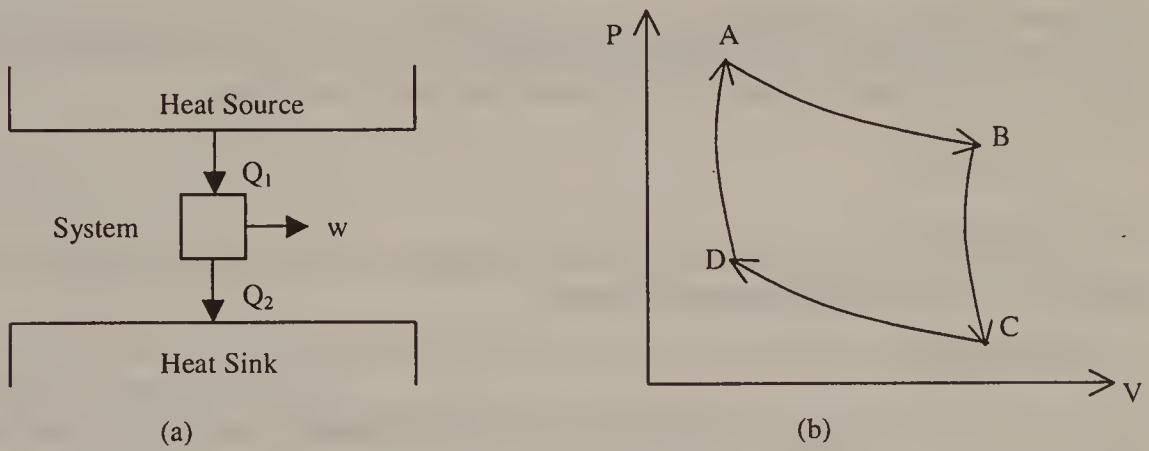


Fig.1.1. (a) Carnot Engine and (b) Carnot Cycle

The statement of the second law is based upon the working of a heat engine. A Carnot heat engine is an idealized engine, in which all steps are reversible. We show the Carnot Cycle for an ideal working gas in Fig.1.1, which operates in four steps. In step AB, the amount of heat Q_1, is absorbed by the gas from the source at temperature T_1. The gas expands isothermally and does work in the process. The next step BC is adiabatic, so the temperature falls to T_2, and further work done. In the next step CD, the heat $(-Q_2)$ given off to the reservoir at lower temperature T_2 and the work is done on the gas. Finally the step DA returns the gas to its original state adiabatically and further work is done on the gas. The efficiency, η, of the reversible engine is defined by

$$\eta = 1 - Q_2/Q_1 = 1 - T_2/T_1 \qquad (1.3.1)$$

For an irreversible engine, however, the efficiency is less than that of a reversible engine, so that

$$\eta = 1 - Q_2/Q_1 < 1 - T_2/T_1 \tag{1.3.2}$$

From (1.3.1) and (1.3.2), we get

$$(Q_1/T_1) + (Q_2/T_2) \leq 0 \tag{1.3.3}$$

This is known as the Clausius inequality for a cycle. The equality sign holds for a reversible cycle. This inequality can be generalized for an arbitrary cycle. Thus

$$\sum_i Q_i/T_i \leq 0 \tag{1.3.4}$$

This expression is called the Clausius inequality and is valid for any cycle.

In the limit of the infinitesimal small cycles, the Clausius inequality can be expressed as

$$\oint dQ/T \leq 0 \tag{1.3.5}$$

where the equality sign hold for reversible cycles.

1.4. Entropy

The Clausius inequality gives the definition of a state property known as entropy of a system. If ΔQ be the quantity of heat absorbed (or liberated) at a temperature T, when a system changes from one state to another, then the change in entropy ΔS of the system is defined by the relation

$$\Delta S = (\Delta Q/T)_R \tag{1.4.1}$$

for a reversible process.

If the states lie very close together and dQ be the quantity of heat absorbed or liberated at the temperature T, then the change in entropy is given by

$$dS = (dQ/T)_R \tag{1.4.2}$$

This is a mathematical expression of the second law. Then the change in entropy of a system for a reversible process from state B to state A is

$$S_A - S_B = \int_B^A (dQ/T)_R \tag{1.4.3}$$

This is a definition of entropy due to Clausius. It gives a method of measuring the change in entropy only. This definition does not give us method of measuring an absolute value of the entropy of the system.

Let us now consider the change in entropy in a reversible cycle. Using the definition of entropy (1.4.2) in the Clausius inequality for a reversible cycle, we get

$$\oint dS = \oint (dQ/T)_R = 0 \tag{1.4.4}$$

Thus the entropy remains constant during a reversible cycle.

Let us consider the change in entropy in an irreversible process. Let a system moves from state A to state B by a reversible process R and return to state A by irreversible process I. These two processes together form a cycle. The Clausius inequality in this case can be written as

$$\oint (dQ/T) = \int_A^B (dQ/T)_R + \int_B^A (dQ/T)_I < 0$$

or

$$\int_B^A (dQ/T)_R > \int_B^A (dQ/T)_I \tag{1.4.5}$$

For a reversible process, the change in entropy is given by

$$S_A - S_B = \int_B^A (dQ/T)_R \tag{1.4.6}$$

Hence the change in entropy for an irreversible process is

$$S_A - S_B > \int_B^A (dQ/T)_I \tag{1.4.7}$$

Combining together (1.4.6) and (1.4.7), the change in entropy for any process is given by

$$S_A - S_B \geq \int_B^A (dQ/T) \tag{1.4.8}$$

Or in differential form

$$dS \geq (dQ/T) \tag{1.4.9}$$

Thus the entropy of the system always increase in an irreversible process and in the limiting case of reversible process ds = (dQ/T).

When we consider an isolated system dQ=0 then (1.4.9) gives

$$(dS)_{isolated} \geq 0 \tag{1.4.10}$$

Where the equality sign stands for the reversible process. Thus the entropy of an isolated system either increases or in the limit remains constant. Eq.(1.4.10) is known as the principle of increase of entropy. Thus in the irreversible process the entropy of the system increases and tends to attain a maximum value.

1.5. Thermodynamic Functions

We consider a system undergoing an infinitesimal reversible process from one equilibrium state to another. The first and second laws of thermodynamics gives a single relation

$$dU = TdS - PdV \tag{1.5.1}$$

Thus the internal energy U is regarded as a function of the variable S and V.

Using the relation

$$d(PV) = PdV + VdP \tag{1.5.2}$$

We can write (1.5.1) as

$$dH = TdS + VdP \tag{1.5.3}$$

where

$$H = U + PV \tag{1.5.4}$$

is known as enthalpy. Here H is a function of independent variables S and P in place of S and V.

Again using the relation

$$d(TS) = TdS + SdT \tag{1.5.5}$$

(1.5.1) can be written as

$$dA = -SdT - PdV \tag{1.5.6}$$

where

$$A = U - TS \tag{1.5.7}$$

is called Helmholtz free energy (or Helmholtz function). It is a function of independent variables T and V.

Using (1.5.2) and (1.5.5), we can write (1.5.1) in the form

$$dG = -SdT + VdP \tag{1.5.8}$$

where

$$\begin{aligned} G &= U - TS + PV \\ &= A + PV \\ &= H - TS \end{aligned} \tag{1.5.9}$$

G is known as Gibb's function (or Gibb's thermodynamic potential). It is a function of independent variables T and P.

The quantities U, H, A and G are all known as thermodynamic potentials. They are all extensive properties of the system and have the dimenssions of energy. P, V, T and S are variables, which describe the thermodynamic state of the system.

Since dU, dH, dA and dG are exact differentials, we obtain

$$T = (\partial U/\partial S)_V = (\partial H/\partial S)_P \tag{1.5.10a}$$

$$P = -(\partial U/\partial V)_S = -(\partial A/\partial V)_T \quad (1.5.10b)$$

$$V = (\partial H/\partial P)_S = (\partial G/\partial P)_T \quad (1.5.10c)$$

$$S = -(\partial A/\partial T)_V = -(\partial G/\partial T)_P \quad (1.5.10d)$$

and

$$(\partial T/\partial V)_S = (\partial P/\partial S)_V \quad (1.5.11a)$$

$$(\partial T/\partial P)_S = (\partial V/\partial S)_P \quad (1.5.11b)$$

$$(\partial P/\partial T)_V = (\partial S/\partial V)_T \quad (1.5.11c)$$

$$(\partial V/\partial T)_P = -(\partial S/\partial P)_T \quad (1.5.11d)$$

(1.5.11) are known as Maxwell's four thermodynamic relations.

In an isothermal process, where T is constant, we have from (1.5.6)

$$dA = -PdV$$

or

$$(\partial A/\partial V)_T = -P$$

and from (1.5.8)

$$dG = VdP$$

or

$$(\partial G/\partial P)_T = V$$

Substituting these values in the expression of G, we get

$$G = A - V(\partial A/\partial V)_T \quad (1.5.12)$$

and

$$A = G - P(\partial G/\partial P)_T \quad (1.5.13)$$

In an isobaric process, where P is constant, (1.5.8) gives

$$dG = -SdT$$

or

$$(\partial G/\partial T)_P = -S$$

Thus the entropy is a measure of rate of change of Gibb's function with temperature at constant pressure. Substituting this value in the expression of G, we get

$$H = G - T\,(\partial G/\partial T)_P \qquad (1.5.14)$$

In an isochoric process, where V is constant, (1.5.6) leads to

$$dA = -SdT$$

or

$$(\partial A/\partial T)_V = -S$$

Thus the entropy is a measure of the rate of change of free energy with temperature at constant volume.

Substituting this value of S in the expression of A, we obtain

$$U = A - T\,(\partial A/\partial T)_V \qquad (1.5.15)$$

(1.5.14) and (1.5.15) are known as Gibb's-Helmholtz relations. They are very important relations of thermodynamics.

Since dQ = TdS, the specific heat at constant volume C_V is

$$C_V = (dQ/dT)_V = T(\partial S/\partial T)_V = (\partial U/\partial T)_V \qquad (1.5.16)$$

as TdS = dU + PdV and that at constant pressure C_P

$$C_P = (dQ/dT)_P = T(\partial S/\partial T)_P = (\partial H/\partial T)_P \qquad (1.5.17)$$

since TdS = dH – VdP

Let us consider the entropy S of a system as a function of T and V, then

$$dS = (\partial S/\partial T)_V\,dT + (\partial S/\partial V)_T\,dV$$

Multiplying both sides by T we get

$$TdS = C_V\,dT + T(\partial S/\partial V)_T\,dV \qquad (1.5.18)$$

Using the Maxwell relation

$$(\partial S/\partial V)_T = (\partial P/\partial T)_V$$

(1.5.18) can be expressed as

$$TdS = C_V\,dT + T(\partial P/\partial T)_V\,dV \qquad (1.5.19)$$

This is known as the first TdS equation,.

On the other hand, if S is a function of T and P, then

$$dS = (\partial S/\partial T)_V dT + (\partial S/\partial P)_T dP$$

or

$$TdS = C_P dT + T(\partial S/\partial P)_T dP \quad (1.5.20)$$

Using the Maxwell's relation

$$(\partial S/\partial P)_T = -(\partial V/\partial T)_P$$

(1.5.20) can be expressed as

$$TdS = C_P dT - T(\partial V/\partial T)_P dP \quad (1.5.21)$$

This is known as the second TdS equation.

These TdS equations are very important since they serve as tools to derive many thermodynamic properties of a system.

Equating (1.5.19) and (1.5.21), we get

$$dT = (T/(C_P - C_V))(\partial P/\partial T)dV + (T/(C_P - C_V))(\partial V/\partial T)_P dP \quad (1.5.22)$$

This shows that T is a function of V and P then

$$dT = (\partial T/\partial V)_P dV + (\partial T/\partial P) dP \quad (1.5.23)$$

Comparing (1.5.22) and (1.5.23), we get a result for C_P - C_V as

$$C_P - C_V = T(\partial V/\partial T)_P (\partial P/\partial T)_V \quad (1.5.24)$$

With the help of cyclic relation

$$(\partial P/\partial T)_V (\partial T/\partial V)_P (\partial V/\partial P)_T = -1$$

$$C_P - C_V = -T (\partial P/\partial V)_T (\partial V/\partial T)_P^2 \quad (1.5.25)$$

From this equation, we draw the following conclusions:

(i) The quantity $(\partial P/\partial V)_T$ is always negative whereas $(\partial V/\partial T)_P^2$ is positive, so $(C_P - C_V)$ can never be negative and $C_P > C_V$.

(ii) At $T \to 0$, $C_P \to C_V$, which means that at absolute zero, the two specific heats are equal.

(iii) When $(\partial V/\partial T)_P = 0$, $C_P = C_V$.

(1.5.25) can be expressed in terms of experimentally known quantities such as the co-efficient of volume expansion β and thermal compressibility K_T defined as

$$\beta = 3\alpha = (1/V)(\partial V/\partial T)_P$$

$$K_T = E_T^{-1} = -(1/V)(\partial V/\partial P)_T$$

where α is the co-efficient of linear expansion and E_T is the isothermal elasticity. Then (1.5.25) can be expressed as

$$C_P - C_V = TV\beta^2/K_T \tag{1.5.26}$$

1.6. Third Law of Thermodynamics: Nernst Heat Theorem

From the second law of thermodynamics, we define the entropy of a system upto an arbitrary additive constant. If we take a state O as the reference state of the system, then the entropies of the system in the states α and β are given by

$$S_\alpha(T) = S_\alpha^0 + \int_0^T (C_\alpha/T)\, dT \tag{1.6.1}$$

$$S_\beta(T) = S_\beta^0 + \int_0^T (C_\beta/T)\, dT \tag{1.6.2}$$

using the relation

$$C_\alpha = CT^\alpha$$

where $\alpha > 1$, and C is constant, we get

$$S_\alpha(T) = S_\alpha^0 + (CT^\alpha/\alpha) \tag{1.6.3}$$

$$S_\beta(T) = S_\beta^0 + (CT^\beta/\beta) \tag{1.6.4}$$

These relations show that the entropy approaches constant value as T approaches absolute zero. Further it is found that the constant value at absolute zero is the same regardless of the chemical state. Thus

$$S_\alpha^0 = S_\beta^0 = S^0$$

These facts led Nernst to state that

$$\lim_{T\to 0} \Delta S = S_\alpha^0 - S_\beta^0 = 0 \tag{1.6.5}$$

where $\Delta S = S_\alpha(T) - S_\beta(T)$, i.e. "in any isothermal reversible process, the change in entropy of a condensed system approaches zero as the temperature approaches zero". This is known as the Nernst heat theorem.

Later, Planck concluded that the entropy of all crystalline solids is same at absolute zero. The arbitrary constants of (1.6.1) or (1.6.2) can be taken as zero. Thus according to Planck, it can be stated that "the entropy of a perfect crystal at absolute zero is zero". Mathematically it can be stated as

$$\lim_{T\to 0} S = S^0 = 0 \tag{1.6.6}$$

This statement is known as the third law of thermodynamics.

Nernst's heat theorem is a macroscopic manifestation of quantum effects and can be deduced from quantum statistics, where quantum states are discrete. It can not be proved in purely classical statistics.

Let us discuss the consequence of Nernst's heat theorem. With the help of the second TdS equation, we obtain

$$(\partial S/\partial T)_P = C_P/T$$

$$(\partial S/\partial P)_T = -(\partial V/\partial T)_P$$

giving

$$(\partial C_P/\partial P)_T = T(\partial^2 S/\partial P\partial T)_P = T(\partial^2 S/\partial T\partial P) = -T(\partial^2 V/\partial T^2)_P \qquad (1.6.7)$$

The coefficient of thermal expansion β is expressed as

$$V\beta = (\partial V/\partial T)_P = -(\partial S/\partial P)_T \qquad (1.6.8)$$

Since the entropy S at a temperature T is given by

$$S = \int_0^T (C_P/T)\, dT$$

We can write

$$V\beta = -\int_0^T (\partial C_P/\partial P)_T\, (1/T)\, dT \qquad (1.6.9)$$

Substitution of (1.6.7) into (1.6.9) leads to

$$V\beta = \int_0^T (\partial^2 V/\partial T^2)_P\, dT = [(\partial V/\partial T)_P]_T - [(\partial V/\partial T)_P]_T \qquad (1.6.10)$$

Hence

$$\lim_{T\to 0} \beta \to 0 \qquad (1.6.11)$$

Thus the coefficient of volume expansion β vanishes as T tends to zero.

Similarly, using the first TdS equation it can be shown that

$$\lim (\partial P/\partial T)_V \to 0$$

The most important consequence of Nernst's theorem is the unattainability of absolute zero. In order to obtain the unttainability, we use the experimental expansion of C_P at low temperature, which is expressed as

$$C_P = T^l (\alpha_0 + \alpha_1 T + \alpha_2 T^2 + ...) \qquad (1.6.12)$$

where l is a positive number and α_0, α_1, α_2, ..., are function of P.

Substituting (1.6.12) in (1.6.9), we get

$$V\beta = -T^{l}[(\alpha_0'/l) + (\alpha_1'/(l+1))T + (\alpha_2'/(l+2))T^2 + \ldots] \tag{1.6.13}$$

where $\alpha_0' = \partial\alpha_0/\partial P$, and so on.
Hence

$$\lim_{T\to 0} V\beta/C_P \to -\alpha_0'/\alpha_0 \tag{1.6.14}$$

which is not zero but a finite quantity. This clearly indicates that a system can not be cooled to absolute zero by a finite change of the thermodynamic parameters.

This is the principle of unattainability of absolute zero. It is some time stated as an alternate form of the third law of thermodynamics.

1.7. General Conditions for Equilibrium

A system interacts with the surrounding due to which its internal state changes. The interaction is partly thermal and partly mechanical. In other words, the interaction consists in a flow of heat from one part of the system to the other and the performance of work by the one part on the other.

When there is no unbalanced force in the interior of the system, and also between the system and its surrounding, the system is said to be in a state of mechanical equilibrium. In such a state all parts of the system are at the same pressure.

When the temperature is uniform throughout the system and is the same as that of its surrounding, then the system is said to be in a state of thermal equilibrium. In this state, no heat flows from one part of the system to the other.

In addition to its interaction with the surrounding, there may be the mutual interaction among the particles constituting the system. When the system does not show any tendency to undergo physical or chemical changes (reactions) due to its mutual interaction, it is said to be in chemical equilibrium.

A system said to be in thermodynamical equilibrium if it is in mechanical, thermal and chemical equilibrium.

Let us derive the condition of equilibrium. The state of a system in the equilibrium condition can be represented by specifying its temperature, pressure and volume, which are independent of time. In general the entropy of a system in equilibrium depends on the internal energy U, volume V and the number of particles, N_i, of species i of the system. In other words

$$S = S(U, V, N_i) \tag{1.7.1}$$

Let us consider two bodies in equilibrium with each other forming a closed system, then

$$U = U_1 + U_2 = \text{Constant} \tag{1.7.2}$$

$$V = V_1 + V_2 = \text{Constant} \tag{1.7.3}$$

$$N_i = N_{i1} + N_{i2} = \text{Constant} \tag{1.7.4}$$

so that

$$\partial U = \partial U_1 + \partial U_2 = 0 \tag{1.7.5}$$

$$\partial V = \partial V_1 + \partial V_2 = 0 \tag{1.7.6}$$

$$\partial N_i = \partial N_{i1} + \partial N_{i2} = 0 \tag{1.7.7}$$

The entropy of the closed system is

$$S = S_1 + S_2 \tag{1.7.8}$$

The entropy of this system in equilibrium has its maximum value, we have

$$\partial S = \partial S_1 + \partial S_2 \tag{1.7.9}$$

From (1.7.1), we get

$$\partial S = (\partial S/\partial U)\delta U + (\partial S/\partial V)\delta V + (\partial S/\partial N_i)\delta N_i \tag{1.7.10}$$

With the help of (1.7.10), (1.7.9) can be written as

$$(\partial S_1/\partial U_1)\delta U_1 + (\partial S_1/\partial V_1)\delta V_1 + (\partial S_1/\partial N_{i1})\delta N_{i1} + (\partial S_2/\partial U_2)\delta U_2 + (\partial S_2/\partial V_2)\delta V_2 + (\partial S_2/\partial N_{i2})\delta N_{i2} = 0$$

Using (1.7.5) – (1.7.7), it can be written in the form

$$[(\partial S_1/\partial U_1) - (\partial S_2/\partial U_2)]\,\delta U_1 + [(\partial S_1/\partial V_1) - (\partial S_2/\partial V_2)]\delta V_1 + [(\partial S_1/\partial N_{i1}) - (\partial S_2/\partial N_{i2})]\,\delta N_{i1} = 0 \tag{1.7.11}$$

As δU_1, δV_1 and δN_{i1} are arbitrary variations, the coefficients of each variation must be zero. Thus we have

$$\partial S_1/\partial U_1 = \partial S_2/\partial U_2 \quad \text{thermal equilibrium} \tag{1.7.12}$$

$$\partial S_1/\partial V_1 = \partial S_2/\partial V_2 \quad \text{mechanical equilibrium} \tag{1.7.13}$$

$$\partial S_1/\partial N_{i1} = \partial S_2/\partial N_{i2} \quad \text{chemical equilibrium} \tag{1.7.14}$$

We define temperature T by

$$T = \partial S/\partial U \tag{1.7.15}$$

then in thermal equilibrium

$$T_1 = T_2 \tag{1.7.16}$$

Let us define pressure P as

$$P = T\,(\partial S/\partial V)_{U,N} \tag{1.7.17}$$

then, along with the thermal equilibrium, the condition to the mechanical equilibrium is

$$P_1 = P_2 \tag{1.7.18}$$

Next, we define a quantity μ_i by the relation

$$\mu_i = -T\,(\partial S/\partial N_i)_{U,V} \tag{1.7.19}$$

then at constant temperature, the condition for the chemical equilibrium is

$$\mu_{i1} = \mu_{i2} \tag{1.7.20}$$

The quantity μ_i is known as the chemical potential of species i.

1.8. Thermodynamics of Phase Transitions

Matter usually exists in the solid, liquid and gas phases. Phase transition is the transition of matter from one phase to another which coexists with the first. Such transition involves a change in mutual arrangement of molecules and in thermodynamic properties of the system. The phase transition points are classified as follows: the solid-liquid phase transition points is called the 'melting point', the liquid-vapour phase transition point is known as the 'boiling point' and the solid-vapour phase transition point is referred to as the 'sublimation point'. Then we have three important temperatures for ordinary substances: the melting (or freezing) point, the boiling point and the sublimation point. We are all familiar with the boiling point of water, which varies with the surrounding atmospheric pressure. Similarly the melting point varies with the pressure, though the variation in this case is not rapid.

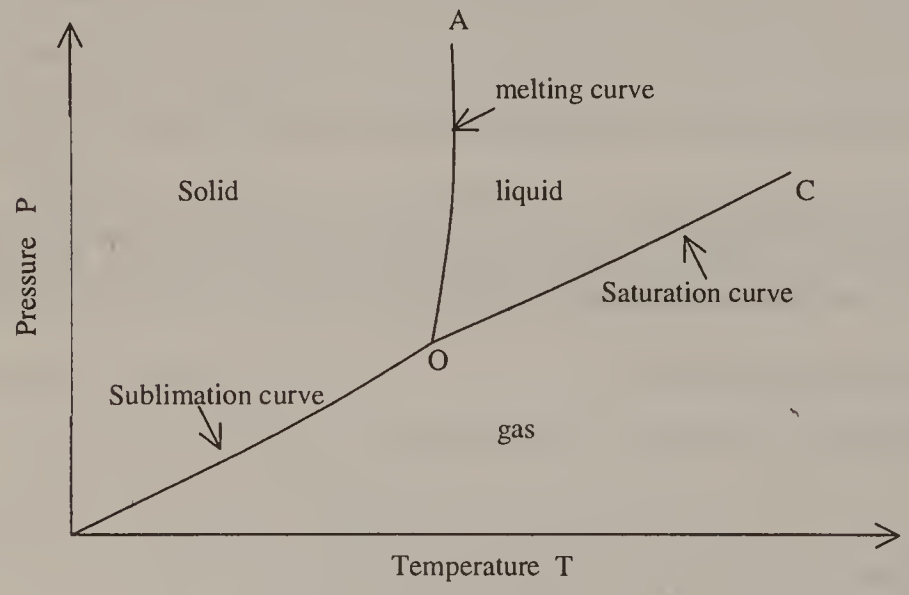


Fig.1.2. P-T phase diagram of one-component system

To specify phase transition boundary it is important to refer a diagram of state which describes the relationship between pressure, volume and temperature. A P-T diagram for a one-component system is given in Fig.1.2. The three phases may be in equilibrium only at a definite temperature and pressure

specific to a given system. It follows from the figure that the line OB represents the 'sublimation' boundary for the system, the line OA the 'melting' boundary and the line OC the 'boiling' boundary, which usually called the 'saturation' boundary. The liquid and gaseous states are separate only over a certain region of P-V-T space. At high temperature and pressure, these two states become one. In Fig.1.2 the saturation line OC terminates at a point C referred to as the 'Critical point'.

On the P-T diagram, the state in which three phases co-exist is represented on the base boundary line by a point, the so-called 'triple-point'. Some substances of this kind can obviously have several triple points.

In a two-phase system, the phases are in equilibrium at the same temperature. In order to transition from the liquid phase to the gaseous phase, a system must receives heat without changing the temperature. This heat is spent to change the phase state of the system and is known as the latent heat or the heat of phase transition.

Let us consider two phases 1 and 2 in equilibrium. The first order phase transition is accompanied by absorption or liberation of latent heat.

We consider an infinitely small reversible Carnot cycle whose isotherms are at temperatures T and T-dT (Fig.1.3). These two isotherms represent two states of a two-phase system. Let the system absorbs the amount of heat Q_1 in transition from phase 1 to phase 2. During this transition the volume of the system changes from V_2 to V_1 at a pressure P. In the reverse process, the volume changes from V_1 to V_2 at a pressure P-dP, and the system liberates the amount of heat Q_2. Since the heat Q_1 is utilised in the phase transition, Q_1=L, where L is the latent heat of transition.

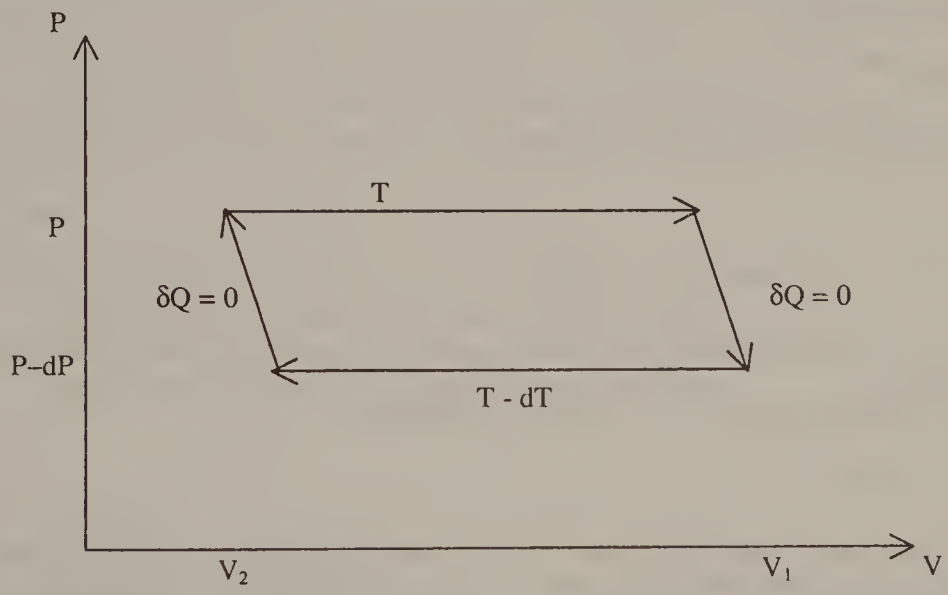


Fig.1.3. Carnot Cycle for derivation of the Clausius-Clapeyron equation

The work done in this cycle will be

$$W = P(V_1 - V_2) + (P - dP)(V_2 - V_1)$$
$$= (V_1 - V_2)\, dP \qquad (1.8.1)$$

Then the efficiency of the cycle is

$$\eta = W/Q_1 = (V_1 - V_2)\, dP / L \qquad (1.8.2)$$

On the other hand, the efficiency of the Carnot cycle is given by

$$\eta = 1 - (T_2/T_1) = 1 - ((T-dT)/T) = dT/T \qquad (1.8.3)$$

Comparing (1.8.2) and (1.8.3), we obtain

$$dP/dT = L / T(V_1 - V_2) \qquad (1.8.4)$$

This equation is known as the Clausius-Clapeyron equation.
(1.8.4) may be used to explain melting, vaporization and sublimation.

In case of the liquid-vapour phase transition, the volume change $\Delta V = V_g - V_l$ is always positive and hence $dP/dT > 0$ i.e. the boiling point increases with increase of pressure. If the vapour pressure is low, $V_g >> V_l$ and (1.8.4) takes the form

$$dP/dT = L_V/TV_g \qquad (1.8.5)$$

where L_V is the latent heat of vaporization. Regarding the vapour as an ideal gas, $V_g = RT/P$ and then

$$dP/P = (L_V/R)\,(dT/T^2) \qquad (1.8.6)$$

On integration, we get

$$\ln [P(T) / P_C(T_C)] = (L_V/R)((1/T_C) - (1/T))$$

or

$$P(T) = P_C(T_C) \exp [(L_V/R)((1/T_C) - (1/T))] \qquad (1.8.7)$$

where P_C and T_C are the critical pressure and critical temperature, respectively, corresponding to the critical point C (Fig.1.2)

For the solid-liquid phase transition, (1.8.4) can be represented as

$$dP/dT = L_m/T(V_l - V_s) \qquad (1.8.8)$$

where L_m is the Latent heat of melting, V_g and V_s are the specific volumes of the liquid and solid phases, respectively, on the melting line. In this case, V_l and V_s are usually close to each other and two cases are possible: (i) the volume change $\Delta V = V_l - V_s$ is positive, then $dP/dT > 0$ and melting point increases with increase of pressure, and (ii) the volume change ΔV is negative, then $dP/dT < 0$ and the melting point decreases with increase of pressure.

In case of the solid-vapour phase transition, (1.8.4) takes the form

$$dP/dT = L_s/T(V_g - V_s) \qquad (1.8.9)$$

where L_s is the latent heat of sublimation, V_g and V_s are the specific volume of vapour and solid phases, respectively, on the sublimation line. In this case $V_g >> V_s$ and $V_g = RT/P$. Then (1.8.9) can be written as

$$dP/dT = (L_s/R)(dT/T^2) \quad (1.8.10)$$

On integration, we get

$$\ln P = -(L_s/RT) + A \quad (1.8.11)$$

Vapour pressures of solids are usually measured over only a small range of temperature. Within this range, (1.8.11) can be expressed in the form

$$\ln P = -(B/T) + A \quad (1.8.12)$$

where A and B are constants of a given system.

In Fig.1.2 the point O is a triple point. It corresponds to the equilibrium between three phases viz solid, liquid and gas. The triple point satisfies the conditions

$$g_s = g_l = g_g \quad (1.8.13)$$

The temperature and pressure corresponding to the triple point are donated by T_r and P_r. For water, they are $T_r = 0.01^\circ C$ and $P_r = 6P_a$. Consequently under normal conditions and atmospheric pressure equilibrium of all phases for water can not be observed at the triple point.

We have briefly revised the salient features of equilibrium thermodynamics which is based on laws of thermodynamics; from which all the thermodynamic (macroscopic) properties can be deduced. However thermodynamics gives no information at all regarding the explanation of thermodynamic properties of the system on the basis of a molecular theory. It is statistical mechanics, that provides a molecular theory of the thermodynamic properties of a macroscopic system. Statistical mechanics will be discussed in the next chapters.

Problems

1.1. A gas obeying the van der Waals equation of state
$(P + (1/V^2))(V - b) = RT$
has $(\partial U/\partial T)_T = a/V^2$. Calculate the internal energy for the gas.

1.2. Apply the first law of thermodynamics to obtain the relation
$C_P - C_V = [(\partial U/\partial V)_T + P](\partial V/\partial T)_P$

1.3. On the basis of the first law of thermodynamics show that
(a) $(\partial U/\partial V)_P = (C_P/V\beta) - P$
(b) $(\partial U/\partial P)_V = (K_T/V\beta) C_V$
(c) $(\partial U/\partial V)_T = ((C_P - C_V)/V\beta) - P$
(d) $(\partial U/\partial T)_P = C_P - PV\beta$

1.4. A gas is defined by the relation
$PV = RT + BP$
and
$(\partial U/\partial V)_T = 0$,
show that
$C_P - C_V = R + 2P(dB/dT)$

1.5. A Cranot engine uses, as a working substance, a gas obeying van der Waals equation of state $(P+(a/V^2))(V - b) = R\theta$ and $(\partial U/\partial V)_T = a/V^2$. Show that the thermodynamic temperature θ is equal to the absolute temperature T.

1.6. Two bodies of unit mass and specific heat C are at temperatures T_1 and T_2, respectively ($T_1 > T_2$). If they are used as a source of heat and sink for a reversible engine, show that the maximum work obtainable from such arrangement is
$C (T_1 + T_2 - 2(T_1T_2)^{1/2})$

1.7. Two bodies of equal mass m and specific C are at temperatures T_1 and T_2 ($T_1 > T_2$). They are brought in thermal contact such that they attain equilibrium temperature. Show that the change in entropy is
$2m\, C \ln [(T_1 + T_2) / 2\sqrt{(T_1T_2)}]$

1.8. The molar specific heat at constant pressure of a substance is given by
$C_P = a + bT + cT^2$
where a, b and c are constants. Calculate the change in entropy when n mole of substance is heated from T_1K to T_2K.

1.9. Derive an expression for the change in entropy when two ideal gases at constant temperature and pressure are mixed.

1.10. Show that the energy of the universe is a constant and the entropy of the universe tends to a maximum.

1.11. The first law of thermodynamics gives the definition of energy while the second law gives the definition of entropy, discuss.

1.12. Define entropy. Show that the change in entropy between two states does not depend on path. Derive an expression for the entropy of a perfect gas in terms of volume, pressure and temperature.

1.13. A mass m of water at temperature T_1 is mixed with an equal mass of water at temperature T_2. Determine the resultant of entropy of the mixture.

1.14. Prove the relations
(i) $TdS = C_V dT + T(\partial P/\partial T)_V\, dV$
(ii) $TdS = C_P dT - T(\partial V/\partial T)_P\, dP$
(iii) $TdS = C_V(\partial T/\partial P)_V\, dP + C_P(\partial T/\partial V)_P\, dV$

1.15. Prove that thermodynamic relations
(a) $(\partial Q/\partial V)_T = T(\partial P/\partial T)_V$
(b) $(\partial Q/\partial P)_T = -T(\partial V/\partial T)_P$

1.16. Prove that for a homogeneous fluid
$C_P - C_V = -T (\partial P/\partial V)_T (\partial V/\partial P)_T^2$
Hence show that $C_P - C_V$ can never be negative.

1.17. Prove the following relations
(a) $C_P - C_V = TV\beta^2 / K_T$
(b) $C_P / C_V = K_T / K_S$
Hence show that
$K_T - K_S = TV\beta^2 / K_T$
where the symbols have their usual meanings.

1.18. Show that for a homogeneous fluid
$C_P - C_V = T (\partial P/\partial T)_V (\partial V/\partial T)_P$
Using this expression, prove that for a van der Waals gas
$C_P - C_V = R + 2a/TV$.

1.19. Derive the formulae
(a) $(\partial C_V/\partial V)_T = T(\partial^2 P/\partial T^2)_V$
(b) $(\partial C_P/\partial P)_T = T(\partial^2 V/\partial T^2)_P$

1.20. Show that a change in temperature during a reversible adiabatic process, when the pressure changes from P_i to P_f is
$\Delta T = (T\langle V\rangle\langle\beta\rangle / C_P) (P_f - P_i)$
where the symbols have their usual meanings.

1.21. Show from the third law of thermodynamics that the specific heat tends to zero as the temperature tends to the absolute zero.

1.22. Show that according to the third law of thermodynamics, the thermal expansion coefficient $(\partial V/\partial T)_P / V$ and pressure coefficient $(\partial P/\partial T)_V$ approach zero as $T \rightarrow 0$.

1.23. State the third law of thermodynamics in terms of entropy difference. Show that it leads to unattainability of absolute zero temperature in a finite number of steps.

1.24. Derive an expression for the change in the boiling point of a liquid with pressure.

1.25. Deduce an expression for the change in melting point of a solid with pressure.

1.26. Show that the latent heat of vaporization of a van der Waals gas is given by
$L_V = -a ((1/V_g) - (1/V_i)) + P (V_g - V_l)$

1.27. Derive the equation
$dP/dT = L_V / T(V_g - V_l)$.
Assuming that L_V is represented by
$L_V = a - bT$
where a and b are constants, show that the pressure of the gas in equilibrium with the liquid is
$P = C T^{-b/R} \exp[-a/RT]$
where C is a constant and R the gas constant.

1.28. Show that
$C_2 - C_1 = (dL/dT) - (L/T)$
where C_1 and C_2 are, respectively, the specific heat of liquid and saturated vapour and L is the latent heat of vaporization.

CHAPTER 2

BASIC PRINCIPLES OF STATISTICAL MECHANICS

2.1. Introduction

In this chapter we discuss the basic principle of statistical mechanics, which studies the macroscopic properties of systems in terms of their microscopic properties. The basic mathematical tool in this approach is the theory of probability, which predicts macroscopic properties from an atomic model of the system.

Statistical mechanics predicts the average value of the thermodynamic (or macroscopic) properties, which differ from the exact value. However, the deviation from the exact value decreases with the increase in the size of the system. In this chapter we discuss the basic principle of statistical mechanics, on which the predictions are nearly correct for a system.

2.2. Macroscopic and Microscopic States

We consider a physical system composed of a large number N of identical particles occupying a large volume V. In a typical case, the magnitude of N and V are of the order of 10^{23}, i.e.

$$N \approx 10^{23} \text{ molecules}$$

$$V \approx 10^{23} \text{ molecular volumes.}$$

These are enormously large numbers, so it is convenient to consider the system in the so-called thermodynamic limit, i.e.

$$V \to \infty$$

$$N \to \infty$$

$$N/V = \rho$$

where ρ is the particle density and is a finite number. In this limit, the extensive properties of the system become directly proportional to the size of the system (i.e. proportional to N or to V), while the intensive properties become independent of them. Of course, the particle density ρ is an important parameter for all the physical properties of the system.

The total energy E of a system consisting of noninteracting particles is equal to the sum of the energies ϵ_i of the individual particles. Thus

$$E = \sum_i n_i \epsilon_i$$

where n_i is the number of particles with energy ϵ_i. Then

$$N = \sum_i n_i$$

According to classical mechanics, the total energy E is continuous. But it is discrete according to quantum mechanics. However, in the thermodynamic limit, where V is large, the spacing of the energy levels is so small that the energy E may be regarded as almost a continuous function. This will be true even for interacting systems. However, in this case the expression for energy will be different.

In the microscopic point of view, the constituent particles of the system are taken into account. In classical mechanics, a state of a system is completely described by coordinates q_i and momenta p_i of all degrees of freedom, and is represented by a representative point in phase space. Such a state of a system is called a microscopic state or microstate.

In the macroscopic point of view, the state of a system, on the other hand, is defined by the parameters N, V and E. The state, thus defined, is the macroscopic state or macrostate of the system. There are a large number of different ways in which the total number N of particles can be arranged in a system. Each of these ways specifies a particular microstate. Obviously, a given macrostate of the system corresponds to a large number of different microstates. Thus, from the microscopic point of view, the macroscopic description of a system cannot be complete. Consequently, we describe the microstates of a macroscopically defined system by prescribing a probability density $\rho(q, p, t)$.

2.3. Phase Space

Let us consider a system of N particles moving according to the laws of classical mechanics. A state of the system is specified by means of 3N position coordinates $q_1, q_2, \ldots, q_{3N}$ and 3N momentum coordinates $p_1, p_2, \ldots, p_{3N}$. The 6N- dimensional space is called the phase space of the system. A point represented by (q_i, p_i), where $i = 1, 2, \ldots, 3N$, represents a particular state of the system in phase space. The point (q_i, p_i) is called a phase point or representative point. If the system is in a gaseous condition, then the phase space is also referred to as the Γ-space and the phase points as the G-points.

Sometimes, the 3N position components are referred to separately as the configurational space and the 3N momentum components as the momentum space. The complete phase space is thus the sum of the configurational space and the momentum space. The phase space is a classical concept.

In course of time, phase point moves in a phase space, generating a phase trajectory in accordance with the laws of mechanics. In statistical mechanics, it is more convenient to use the equation of motion in the Hamilton canonical form as

$$\dot{q}_i = \partial H/\partial p_i$$

$$\dot{p}_i = -\partial H/\partial q_i \ , \quad i = 1, 2, \ldots, 3N \tag{2.3.1}$$

where $H(q, p)$ is the Hamiltonian of the system. By solving these equations, one can find out the location of the phase point at any time t. Along with time, the phase point generates a phase trajectory, whose direction at any time is determined by the velocity vector $v = (\dot{q}_i, \dot{p}_i)$. The locus of all phase points in the phase space satisfying the condition

$$H(q, p) = E$$

defines a surface called the energy surface of energy E. The trajectory always stays on the same energy surface because by definition energy is conserved. On the other hand, if the total energy lies in the

range ($E - \frac{1}{2}\Delta$, $E + \frac{1}{2}\Delta$), the corresponding trajectory will be restricted to the hypershell defined by these limits.

As an example of a phase space, let us consider the motion of a linear harmonic oscillator in a phase space such that the oscillator has a constant energy E given by

$$E = (p^2/2m) + (1/2)\alpha q^2$$

where m is the mass of the oscillator, α a constant and q and p the position and momentum coordinates, respectively. The solutions of Hamiltonian equations for the harmonic oscillator are

$$q = \sqrt{(2E/\alpha)}\,\sin\omega t = q_0 \sin \omega t$$

$$p = m\dot{q} = m\omega q_0 \cos \omega t = p_0 \cos \omega t$$

Hence the phase trajectories are ellipses having a semi-major axis of q_0 and a semi-minor axis of p_0 (Fig.2.1). Each point in the phase space determines a unique phase trajectory. Consequently, phase trajectories cannot interact with one another.

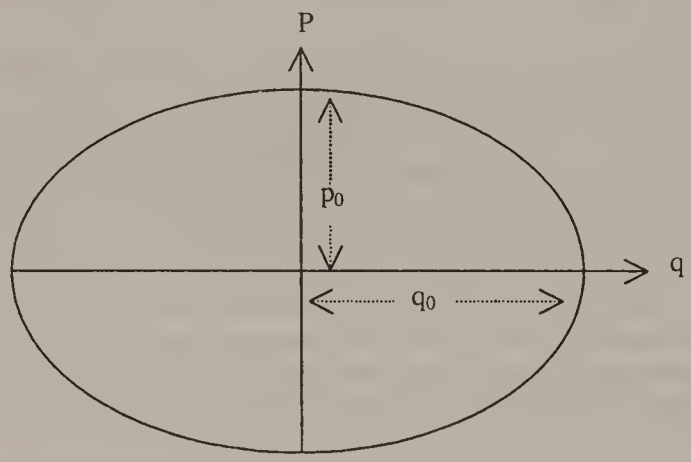


Fig.2.1. Ellipse with semi-major axis q_0 and semi-minor axis p_0.

Now, the thermodynamic property f of a system is a function of generalised coordinates and momenta, i.e. f = f(q, p). A time average of f over a time period T is given by

$$F = (1/T)\int_{t_0}^{T+t_0} f(q,p)dt \qquad (2.3.2)$$

which is measured experimentally. However, such a purely 'mechanical' measurement is quite impossible even for the simple case of a perfectly isolated system. This is due to the complexity of the problem (which has a very large number of degree of freedom). That is why we consider in the next section another method, due to Gibbs, of averaging over dynamical states.

2.4. Statistical Ensemble

J. Willard Gibbs introduced the concept of ensemble for calculating the average values of physical quantities. A collection of similar systems is called an ensemble of systems. Instead of taking time averages, we take averages over this ensemble of systems at one time.

An ensemble of systems is composed of a very large number of systems with the condition that all the systems constituting the ensemble must have the same Hamiltonian, and are assumed to be noninteracting. For example, if we have three balls A, B and C, which are distributed in three boxes 1, 2 and 3 such that each box contains one ball only. These three balls can be distributed in the boxes in 3!= 6 ways. Each distribution is a system and collection of 6 systems forms an ensemble. This ideal can be generalised. Thus if a gas of N molecules is contained in a box of unit volume. These molecules occupy N positions. Hence there are N! number of ways to distribute the molecules in space. Each arrangement of molecules is referred to a system and collection of such systems is an ensemble, which is geometrically represented by a distribution of representative points in Γ-space, usually a continuous distribution.

An ensemble is in fact a mental picture introduced to replace time averages over a single system by ensemble averages, which are averages at a fixed time over all systems in an ensemble. The equivalence of the two types of averages is the subject of ergodic theory, which is not discussed here.

Let us now calculate the ensemble average of a physical quantity. This is expressed in terms of a density function P(q,p,t). This function P represents the number density of the phase points in the phase space. Let a volume element of the phase space for a system of N particles, be

$$dq\,dp = dq_1\,dq_2 \ldots dq_N\,dp_1\,dp_2 \ldots dp_N \equiv dq^N dp^N$$

then the number of phase points in the volume element dq dp around the point (q,p) of the phase space is

$$P(q,p,t)\,dq\,dp \tag{2.4.1}$$

Integrating over space we get

$$\int P(q,p,t)\,dq\,dp = C \tag{2.4.2}$$

where C is the number of systems in the ensemble.

The probability density in the phase space may be written as

$$\rho(q,p,t) = P(q,p,t) / C \tag{2.4.3}$$

The function ρ is called the statistical distribution function or simply, the distribution function for the system. The probability dW of phase points in the volume element dq dp around the point (q,p) of the phase space is given by

$$dW = \rho(q,p,t)\,dq\,dp \tag{2.4.4}$$

This is the number of phase points in the volume element dqdp at any time t. This function satisfies the normalisation condition

$$\int \rho\,(q, p, t)\,dq\,dp = 1 \tag{2.4.5}$$

The integrations in (2.4.5) extend over the whole of phase space. This simply express the fact that the sum of the probabilities of all possible states must be unity.

The ensemble average <f> of a physical quantity f(q,p) is defined as

$$\langle f \rangle = \int f(q, p)\, \rho(q,p,t)\, dq\, dp \tag{2.4.6}$$

The integrations in (2.4.6) also extend over the whole of phase space. In general, the ensemble average <f> may be a function of time. However, if ρ does not depend on time explicitly, i.e.

$$\partial\rho/\partial t = 0$$

then the ensemble average <f> will be independent of time. Such an ensemble is said to be stationary, and represents a system in equilibrium.

Let us consider any two subsystems, that are independent of each other. Let $dq^{(1)}\, dp^{(1)}$ and $dq^{(2)}\, dp^{(2)}$ be volume elements in their phase space. If we regard the two subsystems together as one composite system, then the probability of the composite system in its volume element

$$dq^{(12)}\, dp^{(12)} = dq^{(1)}\, dp^{(1)}\, dq^{(2)}\, dp^{(2)}$$

will be given by

$$dW_{12} = \rho_{12}\, dq^{(12)}\, dp^{(12)} = \rho_1\, dq^{(1)}\, dp^{(1)}\, \rho_2\, dq^{(2)}\, dp^{(2)}$$

or

$$\rho_{12} = \rho_1\, \rho_2 \tag{2.4.7}$$

where ρ_{12} is the distribution function of the composite system and ρ_1, ρ_2 the distribution functions of the separate subsystems. A similar relation is valid for a set of several subsystems. Thus

$$\rho_{12\ldots n} = \prod_{i=1}^{n} \rho_i \tag{2.4.8}$$

If f_1 and f_2 are two physical quantities of two different subsystems, then the mean value of $f_1 f_2$ is

$$\langle f_1 f_2 \rangle = \int f_1 f_2\, \rho_{12}\, dq^{(12)}\, dp^{(12)}$$

$$= \langle f_1 \rangle \langle f_2 \rangle \tag{2.4.9}$$

This can be generalised even for a set of physical quantities belonging to different subsystems.

2.5. Fluctuation

It is the mean value of a physical quantity f, which we measure in the statistical mechanics. The physical quantity itself differs in general from its mean value (see Fig.2.2). The average fluctuation of a physical quantity from its mean value is

$$\langle \Delta f \rangle = \langle f - \langle f \rangle \rangle \tag{2.5.1}$$

The quantity defined in this way is called the average absolute fluctuation.

In course of time, the quantity f varies, fluctuating about its mean value <f>. Since the deviation $f - \langle f \rangle$ is alternately positive and negative, the average absolute fluctuation is zero, and is not suitable. Hence we prefer to use the mean square fluctuation, defined by

$$\langle (\Delta f)^2 \rangle = \langle [f - \langle f \rangle]^2 \rangle$$

$$= \langle f^2 \rangle - \langle f \rangle^2$$

This quantity is called the dispersion of the physical quantity f. It is determined by the difference between the mean square of the quantity and the square of its mean. Hence the root mean

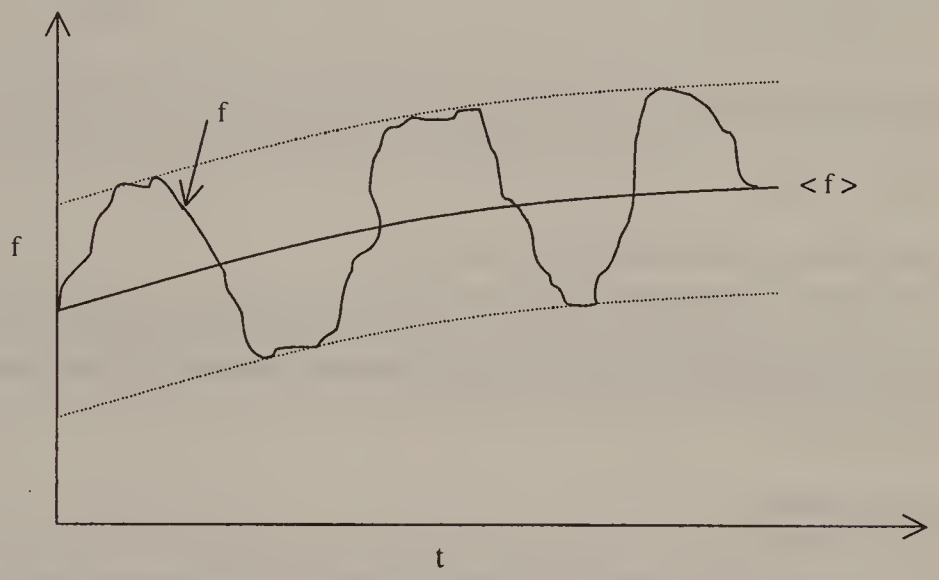


Fig.2.2. The mean value <f> is represented by solid line and true value by irregular line.

square (rms) fluctuation of the quantity f is given by

$$\delta f = \sqrt{\langle (\Delta f)^2 \rangle} = \sqrt{(\langle f^2 \rangle - \langle f \rangle^2)} \qquad (2.5.2)$$

The ratio $\delta f / \langle f \rangle$ is called the relative fluctuation of the quantity f.

Let us assume that a physical quantity f of a body is the sum of its values for the various subsystems of the body. We further assume that the physical quantity is additive.

Let the body be divided into a large number n of approximately equal parts, then

$$f = \sum_{i=1}^{n} f_i$$

where f_i is the physical quantity of the ith subsystem. Hence its mean value is

$$\langle f \rangle = \sum_{i=1}^{n} \langle f_i \rangle \qquad (2.5.3)$$

It is clear that $\langle f \rangle$ increases approximately in proportion to n as n increases.

The rms fluctuation in this case is given by

$$\delta f = \sqrt{<(\Delta f)^2>} = \sqrt{(< [\sum_i \Delta f_i]^2 >)}$$

Using (2.5.1) the mean value of the product $\Delta f_i \, \Delta f_j$ is

$$< \Delta f_i \, \Delta f_j > = <\Delta f_i><\Delta f_j> = 0 \qquad (i \neq j)$$

since each $< \Delta f_i > = 0$. Hence

$$\delta f = \sqrt{(\sum_{i=1}^{n} < (\Delta f_i)^2 >)} \tag{2.5.4}$$

This also increases in proportional to $\sqrt{n}$, as n increases. Therefore, the relative fluctuation is

$$\delta f / <f> \quad 1/\sqrt{n} \tag{2.5.5}$$

Thus the relative fluctuation is inversely proportional to $\sqrt{n}$.

When we consider a homogeneous body to be divided into a large number of small parts of a given size, the number of parts will be proportional to the total number N of particles in the body, i.e. $n \propto N$. Hence the relative fluctuation in this case is inversely proportional to $\sqrt{N}$. Thus we conclude that when the number of particles in a system is sufficiently large, the mean value of a physical quantity f is equal to its exact value.

2.6. Liouville's Theorem

We consider the distribution function ρ of phase points in the phase space, which can describe appropriately an ensemble at any instant. This function ρ will, in general, change with time due to the motion of phase points in the phase space in accordance with the principle of mechanics.

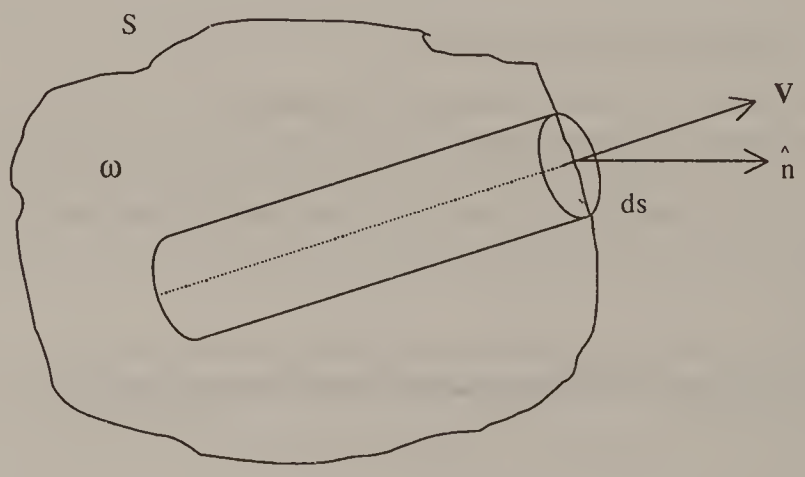


Fig.2.3. Volume ω in the phase space enclosed by surface S.

The motion of phase points in the phase space may be regarded as the motion of a phase space fluid in 2s-dimensional space in analogy to the motion of an ordinary fluid in three-dimensional space. Since the total number of phase points in an ensemble is conserved, the total number of phase points leaving any volume in the phase space per second must be equal to the rate of decrease of the number of phase points in the same volume.

To treat this, let us consider an arbitrary volume ω enclosed by a surface S in the phase space. The number of phase points flowing out per second through an element dS of the surface bounding this volume ω is

$$\rho \mathbf{V}.\, d\mathbf{S} = \rho \mathbf{V}.\hat{\mathbf{n}} dS$$

where $\mathbf{V}$ is the velocity vector of the phase points in the region of the surface element dS and $\hat{\mathbf{n}}$ is the (outward) unit normal vector to this element.
Then the total number of phase points flowing out per second is given by

$$\oint \rho \mathbf{V}.\hat{\mathbf{n}} dS \tag{2.6.1}$$

where the integration is taken over the whole of the closed surface surrounding the volume.

Using Gauss's divergence theorem, the surface integral can be transformed into a volume integral as

$$\oint \rho \mathbf{V}.\hat{\mathbf{n}} dS = \int_{\omega} \mathrm{div}(\rho \mathbf{V})\, d\omega \tag{2.6.2}$$

On the other hand, the rate of decrease of the number of phase points in this volume ω is

$$-(\partial/\partial t) \int_{\omega} \rho d\omega \tag{2.6.3}$$

Since the total number of phase points is fixed, we have from (2.6.2) and (2.6.3)

$$\int_{\omega} \mathrm{div}(\rho \mathbf{V})\, d\omega = -(\partial/\partial t) \int_{\omega} \rho d\omega \tag{2.6.4}$$

or

$$\int_{\omega} [\, (\partial\rho/\partial t) + \mathrm{div}(\rho \mathbf{V}) \,]\, d\omega = 0 \tag{2.6.5}$$

This is possible only when the integrand is zero everywhere in the relevant region of the phase space. Thus we have

$$(\partial\rho/\partial t) + \mathrm{div}(\rho \mathbf{V}) = 0 \tag{2.6.5}$$

This is the equation of continuity for the distribution function in the phase space.

For a phase space of 2s-dimension, where variables are the coordinates q_i and momenta p_i and the velocities $\mathbf{V}_i$ are time derivatives $\dot{q}_i$ and $\dot{p}_i$, we have

$$\text{div}(\rho \mathbf{V}) = \sum_{i=1}^{s} [\, (\partial/\partial q_i)(\rho \dot{q}_i) + (\partial/\partial p_i)(\rho \dot{p}_i) \,]$$

$$= \sum_{i=1}^{s} [\dot{q}_i(\partial\rho/\partial q_i) + \dot{p}_i(\partial\rho/\partial p_i)] + \rho \sum_{i=1}^{s} [(\partial \dot{q}_i/\partial q_i) + (\partial \dot{p}_i/\partial p_i)] \qquad (2.6.6)$$

using the Hamiltonian canonical equation

$$\dot{q}_i = \partial H/\partial p_i$$

$$\dot{p}_i = -\partial H/\partial q_i$$

where $H = (Hq, p)$ is the Hamiltonian of the system, we have

$$\partial \dot{q}_i/\partial q_i = \partial^2 H/\partial q_i \partial p_i = -\partial \dot{p}_i/\partial p_i$$

The second term of (2.6.6) becomes zero and the first term is the Poisson-bracket $[H, \rho]$. Thus we have

$$\text{div}(\rho \mathbf{V}) = [H, \rho] \qquad (2.6.7)$$

and, from (2.6.5)

$$(\partial\rho/\partial t) + [H, \rho] = 0 \qquad (2.6.8)$$

Further, since $\rho = \rho(q, p, t)$, the total time derivative of ρ is given by

$$d\rho/dt = (\partial\rho/\partial t) + [H, \rho] = 0 \qquad (2.6.9)$$

This is Liouville's theorem. According to this theorem, the distribution function ρ is constant along the phase trajectories of the phase points. This significant conclusion, obtained from Liouville's theorem, is known as the principle of conservation of the distribution function in phase space. Thus for a system satisfying Hamilton's canonical equation, the phase-space fluid is incompressible.

Finally, with the help of (2.6.9), we may obtain another form of Liouville's theorem, which will be more useful. For this, we consider a region in the phase space

$$\delta\Gamma = \int dq dp \equiv \int dq_1 \ldots dq_s \, dp_1 \ldots dp_s \qquad (2.6.10)$$

which is taken small enough so that the density ρ is regarded as uniform over its extension. Then the number of phase points in this region is

$$\delta N = \rho \delta\Gamma = \rho \int dq dp \qquad (2.6.11)$$

Let us consider the motion of this region in the phase space. Since no phase points can be created or destroyed, so the number of phase points δN in the region of the phase space must remain fixed, i.e

$$d(\delta N)/dt = (d\rho/dt)\,\delta\Gamma + \rho\,(d(\delta\Gamma/dt) = 0 \qquad (2.6.12)$$

According to (2.6.9), $d\rho/dt = 0$. Thus we obtain

$$d(\delta\Gamma)/dt = 0 \qquad (2.6.13)$$

According to Gibbs, this is known as the principle of conservation of extension in phase space. In accordance with this theorem, any extension in the phase space with moving boundaries, retains a constant volume as time passes. However, its shape may, in general, change with time.

For steady flow, where $\partial\rho/\partial t = 0$, we have

$$[H, \rho] = 0 \qquad (2.6.14)$$

This can be rewritten in the form

$$\sum_{i=1}^{s} [(\partial\rho/\partial q_i)\dot{q}_i + (\partial\rho/\partial p_i)\dot{p}_i] = 0$$

or

$$\mathbf{V}.\text{grad}\,\rho = 0 \qquad (2.6.15)$$

So that the system moves on a surface of constant ρ. To satisfy the condition (Eq.2.6.14) ρ, which is explicitly independent of time, should also be independent of the coordinates (q, p), i.e.

$$\rho(q, p) = \text{Const.} \qquad (2.6.16)$$

This means that the phase points are uniformly distributed over the relevant region of the phase space (outside the relevant region, ρ is identically zero).

An ensemble for which ρ is constant along the trajectories in the phase space is known as a stationary ensemble. This will correspond to the equilibrium situation.

2.7. Statistical Density Matrix

We consider a quantum mechanical ensemble of identical systems in situations where the description is incomplete. When the description of the system is incomplete, the state of the system is described by means of what is called a density matrix. A knowledge of this matrix enables us to calculate the mean value of any physical quantity of the system and also the probabilities of various values of such a quantity.

Let us consider a system. At any time t, the state of the system is completely described by the wave function Ψ. This can be expanded in terms of the normalised function Ψ_n as

$$\Psi = \sum_n C_n \Psi_n(q) \qquad (2.7.1)$$

where

$$C_n = \int \Psi_n^* \Psi\, dq \qquad (2.7.2)$$

Here Ψ_n^* is the complex conjugate of Ψ_n The mean value of any quantity f in this state is defined by

$$\langle f \rangle = \int \Psi^* \hat{f} \Psi\, dq$$

$$= \sum_{n,m} C_n^* C_m f_{nm} \tag{2.7.3}$$

where

$$f_{nm} = \int \Psi_n^* \hat{f} \Psi_m \, dq \tag{2.7.4}$$

are the matrix element of the quantity f, corresponding to the transition from state n to state m. Here $\hat{f}$ is the operator corresponding to f.

Let

$$C_n^* C_m = \rho_{mn}$$

then the mean value of f is given by

$$< f > = \sum_{m,n} \rho_{mn} f_{nm} \tag{2.7.5}$$

In general, ρ_{mn} is a function of time. The set of quantities ρ_{mn} is the density matrix in the energy representation. It is called the statistical matrix in statistical mechanics.

Let us assume that ρ_{mn} is the matrix element of some statistical operator $\hat{\rho}$. Using the matrix multiplication rule, we have

$$\sum_n \rho_{mn} f_{nm} = (\rho f)_{mm}$$

which is a diagonal matrix element of the operator product $(\hat{\rho}\hat{f})$. Then the mean value $< f >$ becomes the trace of this operator.

$$< f > = \sum_m (\rho f)_{mm} = tr(\hat{\rho}\hat{f}) \tag{2.7.6}$$

The element of the diagonal matrix ρ can be written in the form

$$\rho_{mn} = \rho_n \delta_{mn} \tag{2.7.7}$$

where δ_{mn} is the Kronecker δ-function. The diagonal element ρ_n is the measure of the probability that a system, chosen at random (and at any time) from the ensemble, is found to be in the eigenstate Ψ_n. It will naturally depend upon the corresponding eigenvalue E_n, the precise nature of this dependence is, however, determined by the kind of ensemble we like to construct.

Putting $\hat{f}=1$, Eq.(2.7.6) reduces to

$$tr(\hat{\rho}) = \sum_m \rho_m = 1 \tag{2.7.8}$$

which is the normalisation condition (corresponding to the condition $\sum_m |C_m|^2 = 1$).

We now consider the postulates of quantum statistical mechanics, which are the postulates concerning ρ_{mn}. We consider a macroscopic system containing N particles in a volume V. Let its

energy E_n lie between E and $E+\Delta(\Delta<<E)$. Following are the postulates of quantum statistical mechanics:

(i) Postulates of equal a Priori Probability

$$\rho_{nn} = 1 \qquad (E < E_n < E+\Delta)$$
$$= 0 \qquad (\text{otherwise})$$

(ii) Postulates of Random Phases

$$\rho_{mn} = 0 \qquad (m \neq n)$$

It is clear that the averaging over various Ψ states has been used to change from a complete to an incomplete quantum mechanical description of the system. In Eq.(2.7.5) the averaging has a twofold nature; the averaging due to the probabilistic nature of the quantum description, and the statistical averaging. The former is purely quantum mechanical while the latter is purely statistical required by the incompleteness of our information concerning the system of interest.

The statistical matrix in quantum statistics takes the place of the statistical distribution function in classical statistics.

Finally, we derive a general equation of quantum mechanics, which gives the time derivative of the statistical matrix of any (closed) system. For a closed system the wave function will have the same form being independent of time, but the coefficient C_n will depend on time, which is expressed as

$$C_n(t) = C_n(0) \exp(-iE_nt/\hbar)$$

Thus, we have

$$(d/dt)\, C_n^* C_m = (i/\hbar)\,(E_n - E_m)\, C_n^* C_m \tag{2.7.9}$$

Replacing $C_n^* C_m$ by the statistical matrix ρ_{mn}, we obtain an equation of the form

$$\dot{\rho}_{mn} = (i/\hbar)\,(E_n - E_m)\,\rho_{mn} \tag{2.7.10}$$

With the help of relation

$$(E_n - E_m)\,\rho_{mn} = \sum_l [\rho_{ml} H_{ln} - H_{ml} \rho_{ln}]$$

where H_{mn} are the matrix elements of the Hamiltonian $\hat{H}$ of the system, we obtain

$$i\hbar\dot{\rho}_{mn} = \sum_l [H_{ml}\rho_{ln} - \rho_{ml} H_{ln}]$$

$$= (H\rho - \rho H)_{mn} \tag{2.7.11}$$

Using the commutation notation, Eq.(2.7.10) can be written as

$$i\hbar\dot{\rho} = [\hat{H}\hat{\rho} - \hat{\rho}\hat{H}] = [\hat{H}, \hat{\rho}] \tag{2.7.12}$$

We see that if the time derivative of the statistical matrix is zero, i.e. $\dot{\hat{\rho}} = 0$, then

$$[\hat{H}, \hat{\rho}] = [\hat{H}\hat{\rho} - \hat{\rho}\hat{H}] = 0 \tag{2.7.13}$$

Thus the operator $\hat{\rho}$ commutes with the Hamiltonian of the system. This result is the quantum mechanical analogue of Liouville's theorem.

2.8. The Phase Space and Quantum States

The phase space and quantum states are two different concepts used in classical and quantum theory, respectively. However, one can establish the relation between them in the quasi classical case, which is close to classical mechanics.

For this purpose, we consider a one-dimensional harmonic oscillator. According to classical mechanics, the Hamiltonian of this system is

$$H(q, p) = (p^2/2m) + (1/2)Kq^2 \tag{2.8.1}$$

where m is the mass of the particle and K is a constant. The position co-ordinate q and momentum coordinate p of the oscillator are given by

$$q = A \cos(\omega t + \delta)$$

$$p = -m\omega A \sin(\omega t + \delta) \tag{2.8.2}$$

where A is the amplitude and ω the angular frequency of oscillation,

$$\omega = \sqrt{(K/m)}$$

The energy of the oscillator is given by

$$E = (1/2)\, m\omega^2 A \tag{2.8.3}$$

which is a constant of motion.

Eliminating t from the equations of q and p, we obtain

$$(q^2/(2E/m\omega^2)) + (p^2/2mE) = 1 \tag{2.8.4}$$

which is an equation of an ellipse with semi-major axis $\sqrt{(2E/m\omega^2)}$ and semi-minor axis $\sqrt{(2mE)}$. The area of the ellipse is $2\pi E/\omega$. This represents the phase-space trajectory of the phase point (q,p).

Now let us consider the oscillator in the energy range $(E - (1/2)\Delta)$, $(E + (1/2)\Delta)$. The phase point will be confined to a region of the phase space, bounded by two elliptical trajectories corresponding to the energy values $(E + (1/2)\Delta)$ and $(E - (1/2)\Delta)$. The area of this region will be

$$\begin{aligned} \Delta q \Delta p = \iint dq\,dp &= (2\pi(E+(1/2)\Delta)/\omega) - (2\pi(E-(1/2)\Delta)/\omega) \\ &= 2\pi\Delta/\omega \end{aligned} \tag{2.8.5}$$

On the other hand, according o quantum mechanics, the energy values of the harmonic oscillator are given by

$$E_n = \hbar\omega(n + (1/2)) \qquad n = 0, 1, 2, \ldots \qquad (2.8.6)$$

Where n is the vibrational quantum number. Thus the interval between two consecutive energy values in this case is $\Delta = \hbar\omega$.

In the classical picture, the phase point of the system in the phase space will move along one of the trajectories drawn at the energy interval of $\Delta = \hbar\omega$, as shown in Fig.2.4. The area of the phase space enclosed between two consecutive trajectories in this case is simply $2\pi\hbar$. For arbitrary values of E and $\Delta(\hbar\omega \leq \Delta \leq E)$, the number of quantum states is very nearly equal to $\Delta/\hbar\omega$. Hence the area of the phase space of each quantum state is given by

$$(2\pi\Delta/\omega)\,/(\Delta/\hbar\omega) = 2\pi\hbar \qquad (2.8.7)$$

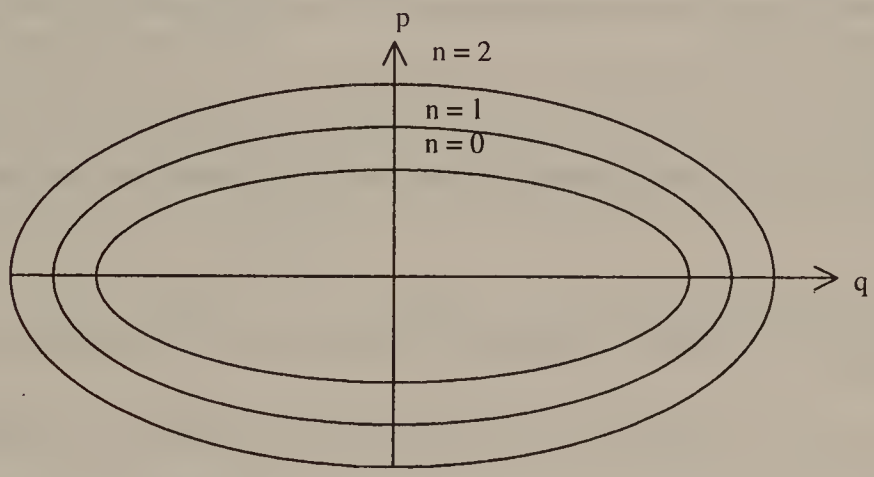


Fig.2.4. Area of the phase space of each quantum state of a linear harmonic oscillator

In other words, the number of quantum states belonging to the volume element (area in this case) $\Delta q\Delta p$ of the phase space is

$$\Delta\Gamma = \Delta q\Delta p/2\pi\hbar \qquad (2.8.8)$$

This quantisation rule can be generalised in case of an arbitrary motion in 2s-dimensional phase space. Thus the volume of the phase space of each quantum state for a system with s degrees of freedom is $(2\pi\hbar)^s$ and there are

$$\Delta\Gamma = \Delta q\Delta p/(2\pi\hbar)^s = \prod_{i=1}^{s} (\Delta q_i \Delta p_i)(2\pi\hbar)^s \qquad (2.8.9)$$

quantum states in a volume element of the phase space.

2.9. Equilibrium Statistical Ensemble

We have seen that for a system in thermodynamic equilibrium, the distribution function ρ in phase space must not depend explicitly on time. For such a system, where $\partial\rho/\partial t = 0$, we have

$$[H, \rho] = 0 \qquad (2.9.1)$$

From classical classical mechanics we know that a quantity which satisfies Eq.(2.9.1) must be an integral of motion or a function of integrals of motion. There exists only seven independent additive integrals of motion – energy, three-components of the momentum, and three-components of the angular momentum. However, for a system with a fixed volume, the energy is the only integral of motion which plays a decisive role in the overall behaviour of any system. Hence, we may assume that the distribution function in the phase space in equilibrium depends only on the energy, i.e. we may assume that

$$\rho(X) = \phi(H(X)) \tag{2.9.2}$$

Here X stands for q and p.

The actual form of the function $\phi(H)$ depends on the type of the system under consideration. We are interested in the following types of systems:

(i) *Adiabatic system*: system, which has a definite energy E and is isolated from the surrounding is called adiabatic. For such a system, the temperature T varies but the volume V and the number of particles N remain fixed.

(ii) *Closed isothermal system*: system which has a fixed temperature T and a fixed number of particles N is called closed isothermal system. For this system, the energy E varies but the volume V remains fixed.

(iii) *Open isothermal system*: system which has a fixed temperature and may exchange particles with the surrounding is known as open isothermal system. For this system, T and V are fixed but E and N vary.

Problems

2.1 What is the difference between a microstate and a macrostate ? Give examples of a microstate and macrostate.

2.2. Explain phase space and quantum state. Show that the volume element of the phase space is given by

$$\Delta\Gamma = \prod_{i=1}^{3N} dq_i\, dp_i$$

Obtain the number of quantum states corresponding to this volume element.

2.3. Calculate the volume Γ in the phase space for:
(a) a harmonic oscillator and
(b) an extreme relativistic particle with energy E enclosed in a box of volume V.

2.4. Obtain an expression for the number of quantum states of a particle in the energy range E and E+dE in both two- and three- dimensional spaces.

2.5. Obtain an expression for the number of quantum states of a relativistic particle with the energy-momentum relation $E = C\sqrt{(p^2+m^2C^2)}$, in the energy range E and E+dE. Discuss the limiting cases of nonrelativistic and extreme relativistic particles.

2.6. Explain statistical ensemble, distribution function and ensemble average.
Show that the relative fluctuation of a system of N particles is inversely proportional to $N^{1/2}$.

2.7. State and prove Liouville's theorem. Discuss its physical significance.

2.8. Discuss the density matrix in statistical mechanics. Obtain Liouville's theorem for quantum statistics.

CHAPTER 3

MICROCANONICAL ENSEMBLE

3.1. Isolated Systems

In this chapter, we consider microcanonical ensembles, for which the system is isolated and does not exchange energy E and particles N with the surroundings. In such a situation, the temperature T varies but the volume V remains fixed.

3.2. Microcanonical Distribution

Let us consider an adiabatic system, which cannot exchange energy with the surrounding when the external parameters are constant. This system has a definite energy E_0, i.e.

$$H(X, a) = E_0 = \text{Constant} \tag{3.2.1}$$

where X denotes coordinates q and momenta p and a represents the external parameters. The distribution function $\phi(E)$, which is a function of energy alone, is defined as

$$\begin{aligned} \phi(E) &= \text{Const.}, \quad \text{if } E_0 - (1/2)\,\Delta E_0 \leq E \leq E_0 + (1/2)\,\Delta E_0 \\ &= 0 \quad \text{otherwise} \end{aligned} \tag{3.2.2}$$

and is represented by the shape of a sharp peak, as shown in Fig.3.1.

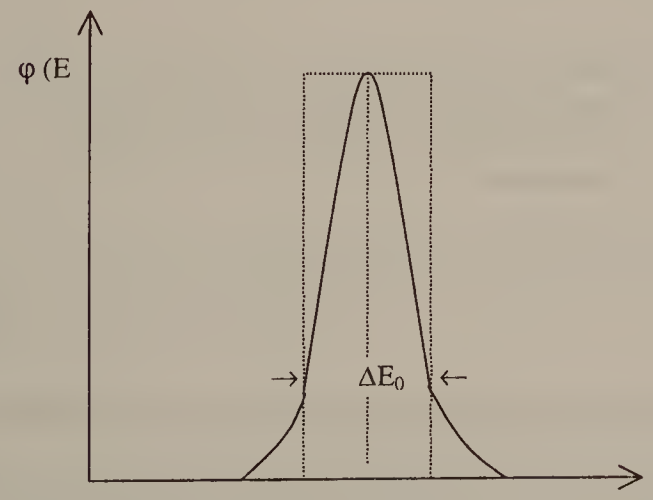


Fig.3.1. The distribution function $\phi(E)$ as a function of E

Since the energy of the system is practically fixed at E_0, $\Delta E_0 \to 0$ and in this limit, $\phi(E)$ approaches

$$\phi(E) = \text{Const. } \delta (E - E_0) \tag{3.2.3}$$

Thus for an adiabatically isolated system, the density distribution function may be written as

$$\rho(X) = (1/\Omega(E_0,a)) \, \delta(E - H(X,a)) \tag{3.2.4}$$

where $\Omega(E_0,a)$ is the normalisation factor, determined by the normalisation condition

$$\int_X \rho(X) \, dX = 1$$

Thus we have

$$\Omega(E_0,a) = \int_X \delta[E - H(X,a)] \, dX \tag{3.2.5}$$

Equation (3.2.4) is called Gibb's microcanonical distribution, which represents an equilibrium system of fixed energy. The ensemble distributed according to this distribution function is called a microcanonical ensemble. It is appropriate for an isolated system because the energy of an isolated system is constant.

In order to give the physical meaning of the quantity $\Omega(E_0,a)$, we integrate it with respect to energy between the energy $E_0 - (1/2)\,\Delta E_0$ and $E_0 + (1/2)\,\Delta E_0$. Thus

$$\Gamma(E_0,a) = \int_{E_0-(1/2)\Delta E_0}^{E_0+(1/2)\Delta E_0} \Omega(E_0,a) dE$$

$$= \int_X \int_{E_0-(1/2)\Delta E_0}^{E_0+(1/2)\Delta E_0} \delta[E - H(X,a)] dE dX \tag{3.2.6}$$

By using the properties of the δ-function

$$\int_{E_0-(1/2)\Delta E_0}^{E_0+(1/2)\Delta E_0} \delta[E - H(X,a)] dE = 1 \qquad \text{if } E_0 - (1/2)\Delta E_0 \le H(X,a) \le E_0 + (1/2)\,\Delta E_0$$

$$= 0 \qquad \text{otherwise}$$

We have from Eq.(3.2.6)

$$\Gamma(E_0,a) = \int_X dX \tag{3.2.7}$$

i.e. $\Gamma(E_0,a)$ is the phase volume enclosed by the energy surface of energy E_0, $= H(X,a)$. From (Eq.3.2.6) we obtain

$$\Omega(E_0,a) = \partial\Gamma(E_0,a)/\partial E \tag{3.2.8a}$$

Thus, $\Omega(E_0,a)$ is the density of the phase volume of the system at the energy E_0. Consequently, $\Omega(E_0,a)dE$ denotes the phase volume of an infinitesimal thin layer enclosed between the energy surface E_0 and E_0+dE, i.e.

$$d\Gamma = \Omega(E_0,a)dE \tag{3.2.8b}$$

The ensemble average of any physical quantity f of an adiabatically isolated system may be calculated by

$$< f > = (1/\Omega(E_0,a)) \int_X f\, \delta[E - H(X,a)]dX \tag{3.2.9}$$

Since we are considering a stationary ensemble, the ensemble average of any quantity must be independent of time. Thus, we finally have

$$< f > = f_{exp} \tag{3.2.10}$$

This bring us to the important conclusion; "the ensemble average of any physical quantity f is identical with the experimental value".

3.3. Principle of Equal a Priori Probabilities

Let us consider the implications of the microcanonical ensemble. We are given an isolated system with constant energy E_0. We known that at a given time the system lies within a certain volume of phase space. The trajectories of phase points passing through this volume trace out a sub-space of the phase space, which we call the accessible region of the phase space. The ensemble is arranged according to Eq.(3.2.4) with constant distribution function in the accessible region of the phase space; outside the accessible region, the distribution function is zero.

In general, all accessible regions of phase space are given equal weights in averaging over a microcanonical ensemble. This is known as the principle of equal a priori probabilities. This is a fundamental postulate of statistical mechanics.

3.4. Entropy

Let us consider a closed system in complete statistical equilibrium. Let the system be divided into a large number of sybsystems. Let $\phi(E)$ be the energy distribution function for any one of them. The function $\phi(E)$ is a function of the energy E of the subsystem and obeys the normalisation condition

$$\int \phi(E)dE = 1 \tag{3.4.1}$$

Thus the area under the curve $\phi(E)$ is unity. The function $\phi(E)$ has a sharp maximum at $E = E_0$ as discussed in Sec.3.2. We may define the 'width' ΔE_0 of the curve $\phi(E)$ as the width of a rectangle of height $\phi(E_0)$, whose area is unity, i.e.

$$\phi(E_0)\, \Delta E_0 = 1 \tag{3.4.2}$$

Let $\Gamma(E,a)$ be a function of energy E. It denotes the volume of phase space in classical statistics and the number of quantum states in quantum statistics. Then the number of quantum states (or the volume elements in phase space) with the energy between E and E+dE can be written as

$$d\Gamma = (\partial\Gamma/\partial E)dE \tag{3.4.3}$$

If $\rho(\Gamma)$ be the density distribution function, then the probability $\phi(E)dE$ that the subsystem has the energy between E and E+dE is $\rho(\Gamma)d(\Gamma)$, i.e.

$$\phi(E)dE = \rho(\Gamma)d(\Gamma) \tag{3.4.4}$$

Hence the energy distribution is

$$\phi(E) = (\partial\Gamma/\partial E)\,\rho(\Gamma) \tag{3.4.5}$$

Substituting this value in Eq.(3.4.2) we have

$$\rho(\Gamma(E_0))\Delta\Gamma = 1 \tag{3.4.6}$$

where

$$\Delta\Gamma = (\partial\Gamma(E_0,a)/\partial E)\,\Delta(E_0) \tag{3.4.7}$$

In quantum statistics, $\Delta\Gamma$ is the number of quantum states corresponding to the energy interval ΔE_0. In classical statistics, $\Delta\Gamma$ is the volume in phase space, corresponding to the interval ΔE_0. Hence

$$\Delta\Gamma = \Delta q\,\Delta p \tag{3.4.8}$$

which has the dimension

$$(\text{momentum x distance})^s = (\text{Action})^s$$

(where s is the number of degrees of freedom).

In case of the quasi-classical system, one can convert the volume in phase space into the number of quantum states as

$$\Delta\Gamma = \Delta q\,\Delta p\,/\,(2\pi\hbar)^s \tag{3.4.9}$$

which is a dimensionless quantity, since a cell of each quantum state has a volume $(2\pi\hbar)^s$.

The quantity $\Delta\Gamma$ is called the statistical weight of the microscopic state of the system. Let us now consider a closed system containing number of noninteracting subsystems. Let $\Delta\Gamma_1$, $\Delta\Gamma_2$, ... be the statistical weights of its subsystems. Then the statistical weight of the closed system is

$$\Delta\Gamma = \prod_i \Delta\Gamma_i$$

or

$$\ln\Delta\Gamma = \sum_i \ln\Delta\Gamma_i \tag{3.4.10}$$

Thus the logarithm of the statistical weight is an additive quantity.

Let us now explain the thermodynamic meaning of the quantity $\Delta\Gamma(E_0,a)$. The differentiation of ln $\Delta\Gamma$ can be written as

$$d(\ln \Delta\Gamma) = (\partial(\ln \Delta\Gamma)/\partial E_0)dE_0 + (\partial(\ln \Delta\Gamma)/\partial a)da$$

$$= (\partial(\ln \Delta\Gamma)/\partial E_0)\,[dE_0 + (\partial E_0/\partial a)da] \qquad (3.4.11)$$

If the external parameter a is the coordinate, the

$$\partial E_0/\partial a = A$$

is the generalised macroscopic force acting in the direction of the coordinate a. Then Eq.(3.4.11) can be written as

$$d(\ln \Delta\Gamma) = (\partial(\ln \Delta\Gamma)/\partial E_0)\,[dE_0 + A\,da] \qquad (3.4.12)$$

Comparing this relation with the fundamental relation of thermodynamics

$$dS = (1/T)\,[dE_0 + A\,da] \qquad (3.4.13)$$

we find the following relations for the entropy S and temperature T.

$$S = k \ln \Delta\Gamma \qquad (3.4.14)$$

$$1/T = (\partial S/\partial E_0) = k\,(\partial(\ln \Delta\Gamma)/\partial E_0) \qquad (3.4.15)$$

where k is the Boltzmann constant, introduced to give unit for entropy. Equation (3.4.14) gives the statistical definition for entropy.

In quantum statistics, the statistical weight is a dimensionless quantity, and hence the entropy thus defined is dimensionless. Since the statistical weight cannot be less than unity, the entropy cannot be negative.

In purely classical statistics, the statistical weight is given by Eq.(3.4.8). The entropy then defined as

$$S = k \ln (\Delta q\, \Delta p) \qquad (3.4.16)$$

would have the dimensions of the logarithm of action. Thus it depends on the choice of unit. However, the change of entropy is independent of the choice of units. Thus, like thermodynamics, the classical statistics gives the definition of the change of entropy between two states.

Only the concept of the number of quantum states enables us to define a dimensionless statistical weight, and hence entropy. In case of classical statistics, this can be achieved by using Eq.(3.4.9) in place of Eq.(3.4.8). Thus, the corresponding expression for S is

$$S = k \ln (\Delta q\, \Delta p / (2\pi\hbar)^s) \qquad (3.4.17)$$

When we consider a closed system containing a number of subsystems, the entropy is given by

$$S = k \sum_i \ln \Delta\Gamma_i = \sum_i S_i \qquad (3.4.18)$$

Thus, the entropy of a composite system is the sum of the entropies of its parts, i.e. entropy is an additive quantity.

Entropy, thus defined, depends on the statistical weight, the precise expression of which is, however, determined by the kind of systems considered.

3.5. Entropy of a Perfect Gas

We consider a microcanonical ensemble of a perfect gas. Let the system consist of N particles, each of mass m, confined in a volume V, and with total energy within the energy range E-δE and E. The volume of the system in the phase space is

$$\Delta q\, \Delta p = \int\int \prod_{i=1}^{N} dq_i\, dp_i$$

and the corresponding number of quantum states is

$$\Delta\Gamma = (1/h^{3N}) \int\int \prod_{i=1}^{N} dq_i\, dp_i \tag{3.5.1}$$

where q's and p's are the position and momentum coordinates, respectively.

Since the particles of a perfect gas are noninteracting, the energy of the system is

$$E = \sum_{i=1}^{N} p_i^2/2m$$

which is independent of the positions of the particles. Thus we have

$$\Delta\Gamma = (V^N/h^{3N}) \int \prod_{i=1}^{N} dp_i \tag{3.5.2}$$

The momentum space integral can be evaluated subject to the constraint condition

$$E - \delta E \leq \sum_{i=1}^{N} p_i^2/2m \leq E \tag{3.5.3}$$

Thus the momentum integral in (3.5.2) is the volume confined between the radii $(2m/E)^{1/2}$ and $[2m(E - \delta E)]^{1/2}$ of 3N-dimensional hypersphere. In the 3-dimensional space, the volume of a spherical hypershell of radii $(2m/E)^{1/2}$ and $[2m(E - \delta E)]^{1/2}$ is

$$\int dp = (4\pi/3) \{ (2mE)^{3/2} - [2m(E - \delta E)]^{3/2} \}$$

$$= (\pi^{3/2}/\Gamma((3+2)/2)) \{ (2mE)^{3/2} - [2m(E - \delta E)]^{3/2} \}$$

In analogy, in the 3 N-dimensional momentum space t he volume of the hypershell of radii $(2m/E)^{1/2}$ and $[2m(E - \delta E)]^{1/2}$ is given by

$$\int \prod_{i=1}^{N} dp_i = (\pi^{3N/2}/(3N/2)!) \{(2mE)^{3N/2} - [2m(E - \delta E)]^{3N/2}\}$$

$$= (\pi^{3N/2}/(3N/2)!)\ (2mE)^{3N/2}\ [1 - (1 - (\delta E/E))^{3N/2}]$$

$$(\pi^{3N/2}/(3N/2)!)\ (2mE)^{3N/2}\ [1 - \exp\ (-(3N/2)(\delta E/E)] \qquad (3.5.4)$$

For a macroscopic system N is very large, hence we can neglect the exponential term in comparison to unity. Thus

$$\int \prod_{i=1}^{N} dp_i = (\pi^{3N/2}/(3N/2)!)\ (2mE)^{3N/2} = (2\pi mE)^{3N/2}/(3N/2)! \qquad (3.5.5)$$

Substituting this value in (3.5.2), we obtain an expression for $\Delta\Gamma$, the statistical weight:

$$\Delta\Gamma = (V^N/(3N/2)!)\ (2m\pi E/h^2)^{3N/2} \qquad (3.5.6)$$

Now the entropy of the system is given by

$$S = k \ln \Delta\Gamma = k \ln [(V^N/(3N/2)!)\ (2\pi mE/h^2)^{3N/2}\ ] \qquad (3.5.7)$$

Using Stirling's formula,

$$\text{Log } N! = N \log N - N \quad = N \log (N/\epsilon)$$

we get

$$S = Nk \ln [V\ (E/N)^{3/2}\ (4\pi m/3h^2)^{3N/2}\ ] + (3/2)\ Nk \qquad (3.5.8)$$

or

$$E = (3h^2N/4\pi mV^{2/3})\ \exp\ ((2S/3Nk) - 1\ ) \qquad (3.5.9)$$

Now let us increase the volume V, the number of particles N, and energy E of the system by a factor α, such that (E/N) remains constant. According to Eq.(3.5.8), the entropy of the new system is

$$S = \alpha\ Nk \ln [\alpha V\ (E/N)^{3/2}\ (4\pi m/3h^2)^{3/2}\ ] + (3/2)\ \alpha Nk$$

$$= \alpha S + \alpha Nk \ln \alpha \qquad (3.5.10)$$

Thus the expression for entropy fails to satisfy the additive property of entropy. This is the so-called Gibbs paradox. In order to get rid of this paradox, we express the entropy as

$$S = k \ln (\Delta\Gamma/N!) \qquad (3.5.11)$$

Then the correct expression for entropy is given by

$$S = Nk \ln [(V/N)(E/N)^{3/2}(4\pi m/3h^2)^{3/2}] + (5/2)Nk \qquad (3.5.12)$$

or

$$E = (3h^2N^{5/3}/4\pi mV^{2/3})\ \exp\ ((2S/3Nk) - (5/3)) \qquad (3.5.13)$$

This expression satisfies the additive property of entropy. Dividing the statistical weight by N!, we take into account the fact that the particles are indistinguishable.

The temperature of the gas is given by

$$T = (\partial E/\partial S)_{N,V} = 2E/3Nk \tag{3.5.14}$$

which establishes a relation between the energy and the temperature. Thus

$$E = (3/2)\, NkT \tag{3.5.15}$$

and the specific heat at constant volume is

$$C_V = (\partial E/\partial T)_V = (3/2)Nk \tag{3.5.16}$$

Substituting (3.5.15) in (3.5.12), we get

$$S = Nk \ln [(V/N)(2\pi mkT/h^2)^{3/2}]+(5/2)Nk \tag{3.5.17}$$

This is the Sackur-Tetrode formula for the entropy of a perfect gas.

3.6. Entropy and Probability Distribution

After having defined entropy, let us now express the probability distribution in terms of it. This can be done using the microcanonical distribution, defined by Eq.(3.2.3)

When we consider a closed system containing a number of subsystems, the probability dW that the system is in the element

$$d\Gamma = \prod_i d\Gamma_i$$

can be written as

$$dW = C.\, \delta (E - E_0) \prod_i d\Gamma_i \tag{3.6.1}$$

where C is a constant and $d\Gamma_i$ denotes the element of quantum states in quantum statistics, or the corresponding volume element in classical statistics. Here $E = \sum_i E_i$, E_i being the energy of the ith subsystem.

Since Γ_i is a function of the energy E_i

$$d\Gamma_i = (\partial \Gamma_i/\partial E_i)dE_i \tag{3.6.2}$$

and dW can be written as

$$dW = C.\, \delta (E - E_0) \prod_i (\partial \Gamma_i/\partial E_i)dE_i \tag{3.6.3}$$

In order to express dW in terms of S_i, we formally assume $\Delta\Gamma_i$, and hence S_i as function of E_i (by definition they are functions of mean energy $\bar{E}_i$). Then the statistical weight $\Delta\Gamma_i$ can be given by

$$\Delta\Gamma_i = (\partial\Gamma_i/\partial E_i)\Delta E_i \tag{3.6.4}$$

Using the definition of entropy along with (Eq.3.6.4), we get

$$\partial\Gamma_i/\partial E_i = \Delta\Gamma_i/\Delta E_i = \exp(S_i/k)/\Delta E_i \tag{3.6.5}$$

Substitution of this value in Eq.(3.6.3) leads to

$$dW = C.\,\delta(E - E_0)\, e^{S/k} \prod_i (dE_i/\Delta E_i) \tag{3.6.6}$$

where S is the entropy of whole closed system

$$S = \sum_i S_i(E_i) \tag{3.6.7}$$

which is assumed to be a function of the energy of its subsystems. Thus the probability dW depends upon the two factors $e^{S/k}$ and $\prod_i \Delta E_i$. However, in comparison to $e^{S/k}$, the effect of $\Pi\Delta E_i$ is negligible, and Eq.(3.6.6) reduces to

$$dW = C\,\delta(E - E_0)\, e^{S/k} \prod_i dE_i \tag{3.6.8}$$

Thus we see that the probablity dW is determined by the entropy of the system, which is the function of the energies of subsystems. This is the most important property of entropy, and is the basis of its application in statistical mechanics.

It is well known that the most probable values of the energies E_i are their mean value $\langle E_i \rangle$. This means that the entropy $S = \sum_i S_i(E_i)$, where $S_i(E_i)$ is a function of E_i, must have its maximum value when $E_i = \langle E_i \rangle$. But at $\langle E_i \rangle$, the system will be in complete statistical equilibrium. Thus we draw the conclusion that the entropy of a closed system in a state of complete statistical equilibrium has its greatest possible value (for a given energy $\sum_i E_i = E_0$ of the system).

We consider a closed system in a non-equilibrium state. Its macroscopic state will vary in time, until the system reaches a state of complete statistical equilibrium. Let the macroscopic state of the system be described by the distribution of energy between the various subsystems. Hence, in course of time, the system passes continuously to states of more and more probable distribution of energy, and finally reaches the most probable state. We can therefore say that a state of complete equilibrium corresponds to the most probable state of the system.

We have seen that the probability is proportional to exp(S/k) where S is the entropy of the system. Hence, the increase in probability increases the entropy of the system. This leads to the conclusion that the processes, in a closed system in non-equilibrium, occur in such a way that the system continuously passes from a state of lower value to a state of higher value, and finally reaches the state of the maximum value of entropy. This maximum value of entropy corresponds to complete statistical equilibrium.

Thus, if a closed system is in a nonequilibrium state at any time, where it does not have a maximum value of entropy, then there is a steady increase in the entropy of the system at a later time. This is the law of increase of entropy, first discovered by Clausius, and later explained by Boltzmann. Thus, we can define the law of increase of entropy in the following way- *"if the entropy of a closed system does not have its maximum value at any time, then the entropy will increase or at least remain*

constant at a later time". It will never decrease. Accordingly, the processes involving macroscopic systems are either irreversible or reversible. In irreversible processes, the entropy of the closed system increases. Reversible processes are those in which the entropy remains constant.

3.7. Nernst's Heat Theorem

Nernst's heat theorem states that the entropy of any body vanishes at absolute zero of temperature, i.e

$$S = 0 \quad \text{at} \qquad T = 0 \tag{3.7.1}$$

This is also called the third law of thermodynamics. We know that the entropy of a system is defined as

$$S = k \ln \Delta\Gamma \tag{3.7.2}$$

where $\Delta\Gamma$ is the statistical weight of the body, which is a pure number according to quantum statistical mechanics. The statistical weight is an increasing function of energy, and the energy is a monotonically increasing function of temperature. Consequently, when the temperature falls, the energy decreases monotonically, and hence the statistical weight decreases. Obviously, when temperature has its least possible value, the body must be in the state of least possible energy.

Hence at absolute zero of temperature the body must be in the lowest quantum state, i.e. in the ground state, where the statistical weight $\Delta\Gamma$ is equal to unity. Therefore, the entropy of the body is zero at absolute zero. Thus, the statistical approach provides a theoretical basis for Nernst's heat theorem.

Nernst's heat theorem is a macroscopic manifestation of quantum effects and can be deduced from quantum statistics, where quantum states are discrete. It cannot be proved in purely classical statistics.

Problems

3.1 What do you understand by a microscopic ensemble. Obtain an expression for the normalising factor $\Omega(E_0,a)$. Discuss its physical significance.

3.2 Define entropy. Discuss its statistical interpretation. Also explain the law of increase of entropy.

3.3 The volume of a perfect gas of N atoms is doubled, the energy being held constant. Show that the change in entropy is
$\Delta S = Nk \ln 2$

3.4 State and prove Nernst's theorem.

CHAPTER 4

CANONICAL ENSEMBLE

4.1. Systems at Fixed Temperature

In the preceding Chapter, we studied the microcanonical ensemble in which the macrostate of the systems is defined by the fixed number of particles N, fixed volume V, and fixed energy E. However, for most physical systems, the concept of a fixed energy (or even a fixed energy range) does not appear satisfactory, as the total energy E of a system is hardly ever measured. It is convenient to keep a fixed temperature T of the system in place of a fixed energy E. For this purpose, the system is placed in contact with an appropriate heat reservoir (or thermostat). Now, an infinitely large number of mental copies of a given system in thermal contact with a heat reservoir form an ensemble in which the macrostate of the system is defined by the fixed parameters N, V and T. Such an ensemble is called a canonical ensemble. On the other hand, the microcanonical ensemble describes systems which are perfectly isolated.

In a canonical ensemble, the energy E of a system is necessarily variable. However, the system in contact with the reservoir forms a composite system, whose energy is fixed. Such a composite system is described by the microcanonical ensemble.

4.2. Canonical Distribution

Let us consider an isolated system, i.e. a system in equilibrium with a heat reservoir (thermostat) having a common temperature T. The composite system is a large closed system, which has the constant energy E. Let A be the system under consideration and B the thermostat. Suppose that the system and the thermostate consist of N_1 and N_2 particles, respectively, and have energies E_1 and E_2; then

$$N_1 + N_2 = N = \text{Constant}$$

$$E_1 + E_2 = E = \text{Constant}$$

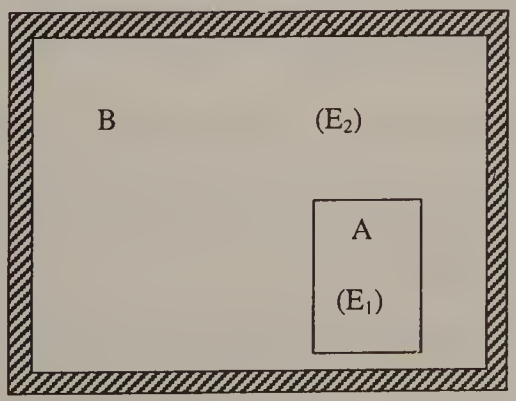


Fig.4.1. System A immersed in a heat reservoir (thermostat) B in equilibrium

Since the thermostate is supposed to be much larger than the system,

$$N_1 << N_2$$

$$E_1 << E_2$$

The composite system is considered as adiabatically isolated. Hence the microcanonical distribution is applicable to such a system. Then probability dW that the system and reservoir are in the volume elements $d\Gamma_1$ and $d\Gamma_2$, respectively, is given by

$$dW = C\,\delta(E_1 + E_2 - E_0)\,d\Gamma_1\,d\Gamma_2 \tag{4.2.1}$$

where E_0 is the given value of the energy of the closed system, which is equal to $E_1 + E_2$, and C is a constant.

Let us find out the probability ρ_n that the system A is in a definite quantum state with energy E_n. In this case $E_1 = E_n$ and $d\Gamma_1 = 1$. The probability ρ_n can be obtained by integrating Eq.(4.2.1) with respect to Γ_2. Thus

$$\rho_n = C \int \delta(E_2 - [E_0 - E_n])d\Gamma_2 \tag{4.2.2}$$

Let $\Gamma_2(E_2)$, being the number of quantum states of the thermostate, be a function of E_2, then

$$d\Gamma_2(E_2) = (\partial\Gamma_2/\partial E_2)dE_2 = (\exp(S_2(E_2)/k)/\Delta E_2)dE_2 \tag{4.2.3}$$

where $S_2(E_2)$ is the entropy of the thermostate, and the function of energy E_2 and ΔE_2 is also a function of E_2.

Substituting this value, Eq.(4.2.2) can be written as

$$\rho_n = C \int \delta(E_2 - [E_0 - E_n])\,(\exp(S_2(E_2)/k)/\Delta E_2)dE_2 \tag{4.2.4}$$

Using the properties of the Dirac δ–function, we obtain the result as

$$\rho_n = C\,(\exp(S_2(E_0 - E_n)/k)/\Delta(E_0 - E_n)) \tag{4.2.5}$$

Since the system A is small, its energy E_n is small in comparison with E_0. The variation in ΔE is negligibly small when E varies slightly and so we can write

$$\Delta(E_0 - E_n) = \Delta E_0 = \text{constant}$$

Next, we expand $S_2(E_0 - E_n)$ about E_0 as

$$S_2(E_0 - E_n) = S_2(E_0) - E_n(\partial S_2(E_0)/\partial E_0)$$

$$= S_2(E_0) - (E_n/T)$$

since $\partial S_2(E_0)/\partial E_0 = 1/T$

T being the temperature of the system. Thus we have an expression for ρ_n as

$$\rho_n = A \exp(E_n/kT) \tag{4.2.6}$$

where

$$A = C\,(\exp(S_2(E_0)/k)/\Delta E_0)$$

is a normalisation constant independent of energy E_n, and is given by the normalisation condition

$$\sum_n \rho_n = 1$$

Thus

$$1/A = \sum_n \exp(-E_n/kT) \tag{4.2.7}$$

In classical statistics, a similar expression for Gibbs distribution function in phase space is

$$\rho(q, p) = A \exp(-E(q, p)/kT) \tag{4.2.8}$$

where E(q, p) is the energy of the system as a function of its coordinates q and momenta p. The normalisation constant A is given by the condition

$$\int \rho \, dq \, dp = 1$$

Thus

$$1/A = \int \exp(-E(q, p)/kT)\, dq\, dp \tag{4.2.9}$$

The normalisation constant 1/A defined by either Eq.(4.2.7) or Eq.(4.2.9) is called the canonical partition function (or integral over the states). Let us denote it by Q_N, then

$$Q_N(V,T) = \int \exp(-E(q, p)/kT)\, dq\, dp \qquad \text{(classical)} \tag{4.2.10}$$

$$Q_N(V,T) = \sum_n \exp(-E_n/kT) \qquad \text{(quantum)} \tag{4.2.11}$$

In order to make Q_N dimensionless, the volume element $dq\, dp \left(\equiv \prod_{i=1}^{N} dq_i dp_i\right)$ is expressed in the corresponding number of quantum states by dividing it by h^{3N}, where N is the number of particles in the system. Further, we divide Eq.(4.2.10) by N! in accordance with the rule of correct Boltzmann counting. Thus, the partition function in classical statistics is strictly defined as

$$Q_N(V,T) = (1/N!h^{3N}) \int \exp(-E(q, p)/kT) \prod_{i=1}^{N} dq_i dp_i \tag{4.2.12}$$

In terms of partition function, the Gibbs distribution function is

$$\rho(q, p) = \exp(-E(q, p)/kT)/N!h^{3N} Q_N \quad (4.2.13)$$

The mean value of any physical quantity f using the Gibbs distribution, is given by

$$< f > = \int f \exp(-E(q, p)/kT)dqdp/\int \exp(-E(q, p)/kT)dqdp \quad \text{(classical)} \quad (4.2.14)$$

4.3. Quantum Canonical Partition Function

The statistical operator $\hat{\rho}$ for a closed system is

$$\hat{\rho} = A \exp(-\hat{H}/kT) \quad (4.3.1)$$

If $\{\psi_n\}$ represents a complete set of (properly symmetrised) orthogonal wave functions, appropriate to the system considered, then

$$\rho_n = A \int \psi_n^* \exp(-\hat{H}/kT)\, \psi_n dq \quad (4.3.2)$$

This is one of the most important formulae in statistical mechanics. Eq.(4.3.2) is known as Gibbs canonical distribution, or simply Gibbs distribution for closed system in quantum statistics.

Using normalisation condition

$$\sum_n \rho_n = 1 \quad (4.3.3)$$

the partition function of the system can also be expressed in terms of the wave function ψ_n as

$$Q_N(V,T) = \sum_n \int \psi_n^* \exp(-\hat{H}/kT)\, \psi_n \prod_{i=1}^{N} dq_i \quad (4.3.4)$$

$$= \sum_n \exp(-E_n/kT) \quad (4.3.5)$$

The distribution function in this case is

$$\rho_n = \exp(-E_n/kT)/Q_N \quad (4.3.6)$$

The corresponding statistical operator $\hat{\rho}$ for a closed system is

$$\hat{\rho} = \exp(-\hat{H}/kT)/Q_N \quad (4.3.7)$$

The mean value of any physical quantity of a quantum system, using the Gibbs distribution is given by

$$< f > = \sum_n f_n \exp(-E_n/kT) / \sum_n \exp(-E_n/kT) \quad \text{(quantum)} \quad (4.3.8)$$

In most physical cases, the energy levels of a system are degenerate. Let g_n be the number of states belonging to the same energy value E_n. In such a case, it would be more appropriate to write the partition function as

$$Q_N(V,T) = \sum_n g_n \exp(-E_n / kT) \tag{4.3.9}$$

The corresponding expression for the probability ρ_n that the system be in any of the states with energy E_n will be

$$\rho_n = g_n \exp(-E_n/kT) / \sum_n g_n \exp(-E_n/kT) \tag{4.3.10}$$

Clearly, the probability of a system having energy E_n becomes directly proportional to g_n. Thus, g_n plays the role of a weight factor for the energy level E_n.

4.4. Equipartition Theorem

Let us apply the Gibbs distribution to obtain the equipartition and the virial theorems. We calculate the phase average of the quantity

$$X_i(\partial H/\partial X_j)$$

where H is the Hamiltonian and X_i is either p_i or q_i ($i = 1, 2, ..., 3N$). Using the canonical distribution, we can write the phase average as

$$\begin{aligned} \langle X_i(\partial H/\partial X_j)\rangle &= A \int\int X_i(\partial H/\partial X_j)\, e^{-H/kT}\, dX_1 \ldots dX_i \ldots dX_j \ldots dX_{3N} \\ &= -AkT \int \ldots \int X_i(\partial/\partial X_j)\, e^{-H/kT}\, dX_1 \ldots dX_i \ldots dX_j \ldots dX_{3N} \end{aligned} \tag{4.4.1}$$

Let us first evaluate the following integral

$$\begin{aligned} \int_{X_j} X_i(\partial/\partial X_j)\, e^{-H/kT}\, dX_j &= [X_i\, e^{-H/kT}]_{X_j=-\infty}^{\infty} - \delta_{ij} \int_{X_j} e^{-H/kT}\, dX_j \\ &= -\delta_{ij} \int_{X_j} e^{-H/kT}\, dX_j \end{aligned} \tag{4.4.2}$$

since the first term on the right hand side of this equation is zero, because $H \to \infty$ when $X_j \to \pm\infty$ (in statistical mechanics we consider only such type of systems). Substituting Eq.(4.4.2) in Eq.(4.4.1), we finally obtain

$$\langle X_i(\partial H/\partial X_j)\rangle = kT\delta_{ij} \tag{4.4.3}$$

since from the normalisation condition

$$A \int \ldots \int e^{-H/kT}\, dX_1 \ldots dX_{3N} = 1$$

Eq.(4.4.3) gives a general relation. In the special case, when $X_i = X_j = p_i$ Eq.(4.4.3) takes the form

$$\langle p_i(\partial H/\partial p_i)\rangle \equiv \langle p_i \dot{q}_i \rangle = kT \tag{4.4.4}$$

This is called the equipartition theorem, while when $X_i = X_j = q_i$, it becomes

$$\langle q_i(\partial H/\partial q_i)\rangle \equiv -\langle q_i \dot{p}_i \rangle = kT \tag{4.4.5}$$

This is referred to as the virial theorem because $\Sigma q_i p_i$ is known in classical mechanics as the virial.

Eqs.(4.4.4) and (4.4.5) are meant for one degree of freedom. Adding over all i, we obtain

$$\langle \Sigma_i p_i(\partial H/\partial p_i)\rangle \equiv \langle \Sigma_i p_i \dot{q}_i \rangle = 3NkT \tag{4.4.6}$$

$$\langle \Sigma_i q_i(\partial H/\partial q_i)\rangle \equiv \langle \Sigma_i q_i \dot{p}_i \rangle = 3NkT \tag{4.4.7}$$

From classical mechanics, it is well known that

$$L = T - U$$

$$H = T + U$$

where T and U are the kinetic and potential energies of the system, respectively. Then

$$2T = H + L = \Sigma_i p_i \dot{q}_i$$

and therefore,

$$\langle T\rangle = (1/2)\langle \Sigma_i p_i \dot{q}_i \rangle = (3/2)NkT \tag{4.4.8}$$

Thus the average kinetic energy associated with each degree of freedom is equal to (1/2)kT. This is called the law of equipartition of energy, which was first stated by Boltzmann.

We can apply the equipartition law to calculate the specific heat of an ideal gas with l degree of freedom. In this case the total energy is the sum of the kinetic energies of atoms. The equipartition law predicts that

$$E = (l/2)\,NkT \tag{4.4.9}$$

Then the specific heat at constant volume is

$$C_V = (\partial E/\partial T)_V = (l/2)Nk \tag{4.4.10}$$

and the specific heat at constant pressure is

$$C_P = (1/2)(l+2)Nk \tag{4.4.11}$$

This leads to

$C_V = (3/2)\,Nk$ for monatomic gas

$= (5/2)\,Nk$ for diatomic gas

and

$C_P = (5/2)\,Nk$ for monatomic gas

$= (7/2)\,Nk$ for diatomic gas

The equipartition theorem is valid at high temperatures, where each degree of freedom of the system is freely excited. At a temperature, at which certain degrees of freedom, due to the insufficiency of energy available, are more or less 'frozen' it cannot be valid.

We now consider the implication of formula (4.4.7). The quantity

$$(1/2)\sum_i q_i(\partial H/\partial q_i) \equiv -(1/2)\sum_i q_i A_i = X \tag{4.4.12}$$

is called the virial of clausius. The average virial of a system is

$$\langle X\rangle = -(1/2)\langle\sum_i q_i A_i\rangle = (3/2)\,NkT \tag{4.4.13}$$

where A_i is the generalised force acting on a molecule whose coordinate is q_i.

In case of a classical gas of noninetracting particles, only the restraining force of the walls of the container will act on the system. If the pressure exerted by the gas is P, then it can be shown that the average virial of ideal gas is

$$\langle X\rangle = (3/2)\,PV \tag{4.4.14}$$

Comparing (4.4.13) and (4.4.14), we obtain the well known result for the ideal gas

$$PV = NkT \tag{4.4.15}$$

4.5. Thermodynamic Functions for the Canonical Ensemble

In this section we calculate the thermodynamic functions, such as entropy, energy, and Helmholtz free energy for the canonical ensemble.

In thermodynamics, the entropy is fixed by the energy independently of whether the system is isolated, or in contact with a thermostate. Hence the entropy of the system of the canonical ensemble with mean energy $\langle E\rangle$ will be equal to the entropy of the microcanonical ensemble with the energy $\langle E\rangle$. By definition, the entropy is given by

$$S = k \ln \Delta\Gamma \tag{4.5.1}$$

where $\Delta\Gamma$ is the statistical weight, and is related to the distribution function $\rho(\langle E\rangle)$by

$$\rho(\langle E\rangle)\Delta\Gamma = 1$$

or

$$\Delta\Gamma = 1/\rho(\langle E\rangle) \tag{4.5.2}$$

According to the canonical distribution, we have

$$\rho(\langle E\rangle) = e^{-\langle E\rangle/kT}/Q_N \tag{4.5.3}$$

where Q_N is the canonical partition function. Using these values Eq.(4.5.1) can be written as

$$S = -k \ln \rho(<E>) = (<E>/T) + k \ln Q_N$$

or

$$<E> - ST = -kT \ln Q_N \tag{4.5.4}$$

Here $<E> \equiv U$ is the internal energy and $A = U - ST$ is called the Helmholtz free energy or simply, free energy. Thus, we have

$$A(N, V, T) = -kT \ln Q_N \tag{4.5.5}$$

Equation (4.5.5) provides a link between the macro- and micro- worlds, and is the basic relationship of statistical thermodynamics. The other thermodynamic properties of the system can be obtained from a knowledge of the free energy. Thus

$$P = -(\partial A/\partial V)_{N,T} = kT((\partial/\partial V) \ln Q_N)_{N,T} \tag{4.5.6}$$

$$S = -(\partial A/\partial T)_{N,V} = k((\partial/\partial T)\, T \ln Q_N)_{N,V} \tag{4.5.7}$$

$$U = kT^2 ((\partial/\partial T) \ln Q_N) = -(\partial/\partial\beta)(\ln Q_N) \tag{4.5.8}$$

Finally, we obtain the specific heat at constant volume:

$$C_V = (\partial U/\partial T)_{N,V} = k\beta^2((\partial^2/\partial\beta^2) \ln Q_N)_{N,V} \tag{4.5.9}$$

4.6. Calculation of Free Energy of an Ideal Gas: Gibbs Paradox

Let us consider an ideal gas of N identical particles enclosed in a container of volume V at temperature T. The Hamiltonian of the ideal gas is of the form

$$H(p, q) = \sum_{i=1}^{N} (p_i^2/m) + \sum_{i=1}^{N} u(r_i) \tag{4.6.1}$$

where $u(r_i)$ is the potential of an external field acting on a molecule located at the point. In the absence of the external field $u(r_i)=0$. Here m is the mass of each particle.

The partition function for the ideal gas can be written as

$$Q_N = (1/h^{3N}) \int \ldots \int \exp(-\Sigma_i (p_i^2/2mkT) \prod_{i=1}^{N} dp_i\, dq_i$$

$$= (1/h^{3N}) \prod_{i=1}^{N} \int \exp(-p_i^2/2mkT) dp_i \int dq_i \tag{4.6.2}$$

The integral over the momentum space is evaluated as

$$\int \exp(-p_i^2/2mkT) dp_i = 4\pi \int_0^{\infty} \exp(-p_i^2/2mkT)\, p_i^2 dp_i$$

$$= (2\pi mkT)^{3/2} \tag{4.6.3}$$

and each integral over the position vector is equal to the volume V of the container. Consequently, one has

$$Q_N = V^N (2\pi mkT/h^2)^{3N/2} \tag{4.6.3}$$

This gives the free energy as

$$A = -kT \ln Q_N$$

$$= -NkT \ln V - (3/2)\, NkT \ln (kT) - (3/2)\, NkT \ln(2\pi m/h^2) \tag{4.6.5}$$

Once the free energy is known, the other thermodynamic properties can be easily calculated. Thus

$$S = (\partial A/\partial T)$$

$$= -Nk[\ln V + (3/2) \ln (kT) + (3/2) + (3/2) \ln(2\pi m/h^2)] \tag{4.6.6}$$

$$U = A + ST = (3/2)\, NkT \tag{4.6.7}$$

$$C_V = (3/2)\, Nk \tag{4.6.8}$$

Now let us increase the number of particles N and the volume V of the system by a factor α (i.e. for the new system $N' = \alpha N$ and $V' = \alpha V$). According to (4.6.5) the free energy of the new system is

$$A' = \alpha NkT \ln(\alpha V) - (3/2)\, \alpha NkT \ln(kT) - (3/2)\, \alpha NkT \ln (2\pi m/h^2)$$

$$= \alpha A - \alpha NkT \ln\alpha \tag{4.6.9}$$

Then, the entropy of the new system is

$$S' = \alpha S + \alpha Nk \ln \alpha \tag{4.6.10}$$

The physical quantities like free energy and entropy are additive in nature. But Eqs.(4.6.9) and (4.6.10), due to the presence of $\ln \alpha$, violate the requirement of additivity. This is called Gibbs paradox.

In order to remove the Gibbs paradox, we add a term

$$NkT \ln N \tag{4.6.11}$$

to the equation (4.6.5) of the free energy

This leads to

$$A' = \alpha A \tag{4.6.12}$$

$$S' = \alpha S \tag{4.6.13}$$

Thus, we see that the addition of (4.6.11) to the free energy removes the Gibbs paradox. Hence, the correct expression for A, not displaying Gibbs paradox, should be the sum of (4.6.5) and (4.6.11), i.e.

$$A = -kT \ln [V^N (2\pi mkT/h^2)^{3N/2}] + NkT \ln N \quad (4.6.14)$$

The corresponding partition function should be given by

$$Q_N = V^N (2\pi mkT/h^2)^{3N/2} \exp(-N \ln N) \quad (4.6.15)$$

According to Stirling's formula for large N

$$\ln N! = (N \ln N) - N$$

$$N \ln N$$

giving

$$\exp(-N \ln N) = 1/N!$$

Hence, instead of (4.6.4), the correct expression for the partition function of an ideal gas will be

$$Q_N = (1/N!) V^N (2\pi mkT/h^2)^{3N/2} \quad (4.6.16)$$

Hence the correct expression for the free energy of an ideal gas is

$$A = -kT \ln [(eV/N)(2\pi mkT/h^2)^{3N/2}] \quad (4.6.17)$$

Accordingly, the correct definition of partition function is

$$Q_N = (1/N!h^{3N}) \int \ldots \int e^{-E(q,p)/kT} \prod_{i=1}^{N} dq_i \, dp_i \quad (4.6.18)$$

This expression is exact, and free from any imperfection leading to the Gibbs paradox. Dividing the canonical partition function by N!, we take into account the fact that the particles are indistinguishable.

4.7. Applications

4.7.1. Entropy of a system

In the canonical ensemble, the probability distribution of the system is given by

$$\rho_n = A \exp(-E_n/kT) \quad (1)$$

where E_n is the energy level of the system in the nth state and A is the normalisation constant. The distribution function ρ_n is a function of energy E_n i.e.

$$\ln \rho_n (E_n) = \ln A - E_n/kT \quad (2)$$

The mean value of $\ln \rho_n (E_n)$ can be obtained from (2)

$$\langle \ln \rho_n (E_n) \rangle = \ln A - \langle E \rangle/kT = \ln \rho(\langle E \rangle) \quad (3)$$

Using the relation

$$\rho(<E>)\,\Delta\Gamma = 1$$

the entropy of a system is defined as

$$S = k \ln \Delta\Gamma = -k \ln \rho(<E>) = -k <\ln \rho_n (E_n)> \tag{4}$$

From the definition of the mean value

$$S = -k \sum_n \rho_n \ln \rho_n \tag{5}$$

4.7.2. Thermodynamic properties of a system with energies 0 and ϵ.

The partition function for such a system is

$$Q = 1 + e^{-\epsilon/kT} \tag{1}$$

which is used to calculate the free energy by the relation

$$A = -kT \ln [1 + e^{-\epsilon/kT}] \tag{2}$$

Then entropy is

$$S = -(\partial A/\partial T) = k \ln [1 + e^{-\epsilon/kT}] + (\epsilon/T)\,(1/(e^{\epsilon/kT}+1)) \tag{3}$$

internal energy is

$$U = \epsilon/(e^{\epsilon/kT}+1) \tag{4}$$

and the specific heat at constant volume is

$$C_v = k\,(\epsilon/kT)^2\,(e^{\epsilon/kT}/(e^{\epsilon/kT}-1)^2) \tag{5}$$

At low temperatures $\epsilon/kT >> 1$, therefore Eq.(5) reduce to

$$C_v = k\,(\epsilon/kT)^2\,e^{-\epsilon/kT}$$

leading to

$$C_v \to 0 \text{ when } T \to 0$$

At high temperature $\epsilon/kT << 1$ and (5) takes the form

$$C_v = k\,(1+(\epsilon/kT) + (1/2)(\epsilon/kT)^2 + \ldots)/(1+(1/2)(\epsilon/kT) + \ldots)^2$$

giving

$$C_v \to k \text{ when } T \to \infty$$

4.7.3. A system under a gravitational force

Let us consider a collection of non-interacting particles each of mass m in a volume V where the gravitational force in a negative z-direction. The system is in thermal equilibrium at a temperature T. The Hamiltonian of the system consisting of N such particles is given by

$$H = \sum_{i=1}^{N} [\, (p_i^2/m) + mgz_i \,] \tag{1}$$

where g is the acceleration due to gravity.

The partition function of the system in this case is given by

$$Q_N = [Q_1]^N \tag{2}$$

where Q_1 is the single-particle partition function. Thus using (1), we can write

$$Q_1 = (1/2\pi\hbar) \int\int \exp[-((p_i^2/2m) + mgz_i) / kT]\, dp_i\, dz_i$$

$$= (1/2\pi\hbar) \int_{-\infty}^{\infty} \exp[-p_i^2/2mkT\,]\, dp_i \int_{0}^{\infty} \exp[-mgz_i/kT] dz_i$$

Integrating over the momentum and coordinate, we obtain

$$Q_1 = (1/2\pi\hbar)\, (2mkT)^{1/2}\, (kT/mg) = ((kT)^3/2\pi\, mg\hbar^2)^{1/2} \tag{3}$$

and

$$Q_N = ((kT)^3/2\pi\, mg\hbar^2)^{N/2} \tag{4}$$

Then the free energy of the system is

$$A = -kT \ln Q_N = -(1/2)\, NkT \ln [(kT)^3/2\pi\, mg\hbar^2] \tag{5}$$

Other thermodynamic propperties can be calculated using (5). Thus the entropy is

$$S = -(\partial A/\partial T)_V = (1/2)\, Nk\, [\ln ((kT)^3/2\pi\, mg\hbar^2) + 3] \tag{6}$$

energy is

$$U = A + ST = (3/2)\, NkT \tag{7}$$

and the specific heat at constant volume is

$$C_V = (3/2)\, Nk \tag{8}$$

which is independent of temperature.

4.7.4. Particle in a box

We consider a particle of mass m inside a cubical box of side L and volume V. The energy eigen value for the single particle quantum states are given by

$$\epsilon_i = (\hbar^2/2m)\,(K_x^2 + K_y^2 + K_z^2) \tag{1}$$

where

$$k_x = n_x\pi/L$$

$$k_y = n_y\pi/L \tag{2}$$

$$k_z = n_z\pi/L$$

Here the quantum numbers n_x, n_y and n_z are positive integers greater than zero. Since $V = L^3$, and using (2), we have

$$\epsilon_i = (\pi^2\hbar^2/2mV^{2/3})\,(n_x^2 + n_y^2 + n_z^2) \tag{3}$$

Then the partition function of single particle is

$$Q_1 = \sum_{(\text{states})} \exp(-\beta\epsilon_i) = \sum_{n_x}\sum_{n_y}\sum_{n_z} \exp\left[-C\,(n_x^2 + n_y^2 + n_z^2)\right] \tag{4}$$

where

$$C = \beta\pi^2\hbar^2/2mV^{2/3} \tag{5}$$

The quantum numbers n_x, n_y and n_z can have the positive integer value from 1 to ∞. Eq.(4) can be rewritten in the form

$$Q_1 = \sum_{n_x=1}^{\infty} \exp(-cn_x^2) \sum_{n_y=1}^{\infty} \exp(-cn_y^2) \sum_{n_z=1}^{\infty} \exp(-cn_z^2)$$

$$= Q_1^x\, Q_1^y\, Q_1^z \tag{6}$$

where

$$Q_1^x = \sum_{n_x=1}^{\infty} \exp(-cn_x^2) \tag{7}$$

Changing the summation into the integration, Eq.(7) can be written as

$$Q_1^x = \int_0^{\infty} \exp(-cn_x^2)\, dn_x \tag{8}$$

Let us put $cn_x^2 = x$, then (8) can be written as

$$Q_1^x = (1/2C^{1/2}) \int_0^{\infty} \exp(-x)\, x^{-1/2}\, dx \quad = (1/2)\,(\pi/C)^{1/2} \tag{9}$$

The expressions for Q_1^y and Q_1^z are the same. So Eq.(6) becomes

$$Q_1 = (1/8)(\pi/C)^{3/2} = (m/2\pi\beta\hbar^2)^{3/2} V \tag{10}$$

Eq.(10) is the partition function associated with the translational degree of freedom of a particle in a box. It is derived for a particle in a cubical box. However it is valid for any shape of box.

Then the free energy of the particle in a box is

$$A = -kT \ln Q_1$$

$$= -kT \ln V - (3/2)\, kT \ln (mkT/2\pi\hbar^2) \tag{11}$$

The entropy S is

$$S = k \ln V - (3/2)\, k \ln (mkT/2\pi\hbar^2) + (3/2)k \tag{12}$$

The internal energy U is

$$U = (3/2)\, kT \tag{13}$$

and pressure P

$$P = -(\partial A/\partial V)_T = kT/V$$

Hence

$$PV = kT \tag{14}$$

4.7.5. Linear harmonic oscillators

Let us consider a system of harmonic oscillators, each of mass m, in thermal equilibrium. The oscillators do not interact with one another. We assume that they execute small oscillations with the same frequency ω. The Hamiltonian of the system consisting of N such oscillators is given by

$$H(q, p) = (1/2) \sum_{i=1}^{N} [\, (p_i^2/m) + m\omega^2 q_i^2 \,] \tag{1}$$

where q_i, p_i are, respectively, the generalised coordinates and generalised momenta. This is true in classical mechanics. In quantum mechanics, however, the energy levels of the system are given by

$$E_n = \sum_i \hbar\omega(n_i + (1/2)) \tag{2}$$

where n_i is an integer ($n_i = 1, 2, \ldots$).

We use these two expressions for energy to calculate the thermodynamic properties of the system and compare the results so derived.

The partition function of the system in this case is given by

$$Q_N = [Q_1]^N \tag{3}$$

where Q_1 is the single-particle partition function of an oscillator. Thus using (1), we can write as

$$Q_1 = (1/2\pi\hbar) \int\int \exp[-((p_i^2/2m) + m\omega q_i) / kT]\, dq_i\, dp_i$$

$$= (1/2\pi\hbar) \int_{-\infty}^{\infty} \exp(-p_i^2/2mkT)\, dp_i \int_{-\infty}^{\infty} \exp[-m\omega^2 q_i^2/2kT] dq_i$$

Integrating over the momentum and coordinate, we obtain

$$Q_1 = (1/2\pi\hbar)\, (2\pi mkT)^{1/2}\, (2\pi kT/m\omega^2)^{1/2}$$

$$= (kT/\hbar\omega)^N \tag{4}$$

and

$$Q_N = [kT/\hbar\omega]^N \tag{5}$$

Then, the free energy of the system is

$$A = -kT \ln Q_N = -NkT \ln (kT/\hbar\omega) \tag{6}$$

Other thermodynamic properties can be calculated using (6). Thus the entropy is

$$S = Nk [\ln (kT/\hbar\omega) + 1] \tag{7}$$

energy is

$$U = NkT \tag{8}$$

and specific heat at constant volume is

$$C_V = Nk \tag{9}$$

Thus the mean energy per oscillator is kT in accordance with the equipartition law. The specific heat C_V is independent of temperature.

When (2) is used, the single particle partition function is written as

$$Q_1 = \sum_{n_i=1}^{\infty} \exp(-\hbar\omega(n_i + (1/2))/kT)$$

$$= [\exp(-\hbar\omega/2kT)/(1 - \exp(-\hbar\omega/kT))] = [2\sinh(\hbar\omega/2kT)]^{-1} \tag{10}$$

and complete partition function becomes

$$Q_N = [\exp(-\hbar\omega/2kT)/(1 - \exp(-\hbar\omega/kT))]^N \tag{11}$$

Using (11), the free energy is

$$A = N[(1/2)\hbar\omega + kT \ln(1 - \exp(-\hbar\omega/kT)]$$

$$= NkT \ln [2 \sinh (\hbar\omega/2kT)] \quad (12)$$

Other thermodynamic properties can be given as

$$S = Nk[((\hbar\omega/kT)/(\exp(\hbar\omega/kT) - 1)) - \ln(1 - \exp(-\hbar\omega/kT))]$$

$$= Nk[(1/2)(\hbar\omega/kT) \coth (\hbar\omega/2kT) - \ln 2\sinh (\hbar\omega/2kT)] \quad (13)$$

$$U = N[(1/2) + (\hbar\omega/(\exp(\hbar\omega/kT) - 1))]$$

$$= (1/2) N\hbar\omega \coth (\hbar\omega/2kT) \quad (14)$$

and

$$C_V = Nk (\hbar\omega/kT)^2 (\exp(\hbar\omega/kT)/(\exp(\hbar\omega/kT) - 1)^2)$$

$$= (1/4) Nk (\hbar\omega/kT)^2 \operatorname{cosech}^2 (\hbar\omega/2kT) \quad (15)$$

At low temperatures, $(\hbar\omega/kT) << 1$, and (15) reduces to

$$C_V = Nk (\hbar\omega/kT)^2 \exp(-\hbar\omega/kT) \quad (16)$$

giving

$$C_V \to 0 \text{ as } T \to 0$$

At high temperature, on the other hand, $\hbar\omega/kT << 1$ and (15) takes the form

$$C_V = Nk (1+(\hbar\omega/kT)+...)/(1+(1/2)(\hbar\omega/kT)+ ...)^2 \quad (17)$$

leading to

$$C_V = Nk \text{ as } T \to \infty$$

Thus the classical results are valid only at high temperature.

4.8. Classical Systems

Let us apply the theory developed in the preceding sections to a system, which can be treated classically. For such a system the partition function may be written as the integral over the phase space.

Let us consider a system of N identical particles, each of mass m, enclosed in a container of volume V at a temperature T. The Hamiltonian of the system is the sum of the kinetic energy and potential energy, i.e.

$$H = \sum_i (p_i^2/m) + U(r_1, r_2, \ldots r_N) \tag{4.8.1}$$

where U is the interaction potential of the system. We assume that the potential due to the external field is zero.

The partition function for this system can be written as

$$Q_N = (1/N!h^{3N}) \int \ldots \int e^{-H/kT} \prod_{i=1}^{N} dp_i dq_i \tag{4.8.2}$$

Substituting (4.8.1) in (4.8.2) and carrying out the momentum integration, we get

$$Q_N = (1/N!) (2\pi mkT/\hbar^2)^{3N/2} \int\int e^{-U/kT} \prod_{i=1}^{N} dr_i \tag{4.8.3}$$

or

$$Q_N(V,T) = Z_N / N!\lambda^{3N} \tag{4.8.4}$$

where

$$\lambda = (h^2/2\pi mkT)^{1/2} = (2\pi\hbar^2\beta/m)^{1/2} \tag{4.8.5}$$

and

$$Z_N = Z(N, V, T) = \int\int e^{-U/kT} \prod_{i=1}^{N} dr_i \tag{4.8.6}$$

Here λ is the thermal wavelength of the particles. The function Z_N is generally known as the configuration integral of the system, and $e^{-U/kT}$ is called the Boltzmann factor.

For an ideal gas of noninteracting particles, U = 0, and (4.8.6) reduces to

$$Z_N^{id} = V^N$$

and

$$Q_N(V, T) = V^N/N!\,\lambda^{3N} \tag{4.8.7}$$

It is interesting to note that we may write Q_N for an ideal gas as

$$Q_N(V, T) = (1/N!) [Q_1(V,T)]^N \tag{4.8.8}$$

where

$$Q_1(V, T) = (1/h^3) \int \exp(-p^2/2mkT) dpdr \tag{4.8.9}$$

is the partition function of a single molecule of the system. Equation (4.8.8) is valid even if the molecules have internal degrees of motion as well. The only essential requirement for the validity of (4.8.8) is the absence of interactions among the constituent particles.

Another quantity of importance in constructing the statistical theory is the generic distribution function, which is defined by

$$n_N(r_1, r_2, \ldots r_l) = (N!/(N-l)!) \int\int \rho(r^N, p^N)\, dp^N\, dr^{N-l} \tag{4.8.10}$$

where

$$\rho(r^N, p^N) = e^{-H/kT}/N!\, h^{3N} Q_N \tag{4.8.11}$$

Substituting (4.8.11) in (4.8.10) and integrating over momenta, we get

$$n_N(r_1, r_2, \ldots r_l) = (1/(N-l)!\, \lambda^{3N} Q_N) \int\int e^{-U/kT}\, dr^{N-l} \tag{4.8.12}$$

or

$$n_N(r_1, r_2, \ldots r_l) = (N!/(N-l)!\, Z_N) \int\int e^{-U/kT}\, dr^{N-l} \tag{4.8.13}$$

This is also known as the l-particle density distribution function. The most important distribution function is $n_N(r_1,r_2)$. The quantity $n_N(r_1,r_2)\, dr_1\, dr_2$ measures the probability that one particle of the system is in dr_1 at r_1 and another in dr_2 at r_2. The normalisation of $n_N(r_1, r_2, \ldots r_l)$ is

$$\int n_N(r_1, r_2, \ldots r_l) dr^l = N!/(N-l)! \tag{4.8.14}$$

In particular

$$\int n_N(r_1)\, dr_1 = N \tag{4.8.15}$$

Thus for a homogeneous fluid

$$n_N(r_1) = N/V = \rho \tag{4.8.16}$$

where ρ is the number density.

4.9. Quantum Systems

We now apply the theory developed in the previous section to systems where the quantum effects are important. There are two types of quantum effects.

(i) diffraction effects: These are linked to the wave nature of the particles of the systems, and

(ii) exchange effects: These are due to statistics (Bose-Einstein and Fermi-Dirac) obeyed by the particles.

The exchange or symmetry effects are, in general, very small for all fluids. Diffraction effects, on the other hand, are appreciable even at high temperature.

We consider a quantum mechanical system of N identical particles, each of mass m, enclosed in a container of volume V in equilibrium at temperature T. The Hamiltonian operator of the system is

$$\hat{H} = -(\hbar^2/2m) \sum_{i=1}^{N} \nabla_i^2 + U(r_1, r_2, \ldots r_N) \tag{4.9.1}$$

where U is the total interaction potential and ∇_i^2 is the Laplacian operator of the ith particle. Then, the partition function for the quantum system can be expressed as

$$Q_N(V, T) = \int\int \sum_n \Psi_n^* \exp(-\hat{H}/kT) \Psi_n \prod_{i=1}^{N} dr_i \tag{4.9.2}$$

where Ψ_n is a complete set of (properly symmetrized) orthogonal wave functions of the system.

Let us now introduce a quantity known as the Slater sum, and defined as

$$W_N(\mathbf{r}_1,\mathbf{r}_2,..., \mathbf{r}_N) = N!\, \lambda^{3N} \sum_n \Psi_n^*(\mathbf{r}_1, \mathbf{r}_2, ... \mathbf{r}_N) \exp(-\hat{H}/kT) \Psi_n(\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_N) \tag{4.9.3}$$

Alternatively it is also written as

$$W_N(\mathbf{r}_1,\mathbf{r}_2,..., \mathbf{r}_N) = N!\, \lambda^{3N} \langle \mathbf{r}_1,\mathbf{r}_2,..., \mathbf{r}_N | \exp(-\hat{H}/kT) | \mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_N \rangle \tag{4.9.4}$$

The quantity $W_N(\mathbf{r}_1,\mathbf{r}_2,..., \mathbf{r}_N) \prod_{i=1}^{N} dr_i$ is the measure of the probability that the 'configuration' of a given system is found to be within the interval $(\mathbf{r}_1,..., \mathbf{r}_N)$, $(\mathbf{r}_1+d\mathbf{r}_1,..., \mathbf{r}_N+d\mathbf{r}_N)$. The classical counterpart of the Slater sum is the Boltzmann factor

$$W_N^C(\mathbf{r}_1,\mathbf{r}_2,..., \mathbf{r}_N) = e^{-U/kT} \tag{4.9.5}$$

In terms of the Slater sum, the canonical partition function can be written as

$$Q_N(V, T) = (1/N!\lambda^{3N}) \int ... \int W_N(\mathbf{r}_1,\mathbf{r}_2,..., \mathbf{r}_N) \prod_{i=1}^{N} d\mathbf{r}_i$$

$$= Z_N/N!\lambda^{3N} \tag{4.9.6}$$

where

$$Z_N = \int\int W_N(\mathbf{r}_1,\mathbf{r}_2,..., \mathbf{r}_N) \prod_{i=1}^{N} d\mathbf{r}_i \tag{4.9.7}$$

In quantum statistics, the l-particle density distribution function n_N is defined by

$$n_N(\mathbf{r}_1,\mathbf{r}_2,..., \mathbf{r}_N) = (1/(N-l)!\, \lambda^{3N} Q_N) \int\int W_N(\mathbf{r}_1,\mathbf{r}_2,..., \mathbf{r}_N) \prod_{i=l+1}^{N} d\mathbf{r}_i \tag{4.9.8}$$

$$= (N!/(N-l)!\, Z_N) \int\int W_N(\mathbf{r}_1,\mathbf{r}_2,..., \mathbf{r}_N) \prod_{i=l+1}^{N} d\mathbf{r}_i \tag{4.9.9}$$

The normalisation of n_N is again given by

$$\int n_N(\mathbf{r}_1,\mathbf{r}_2,..., \mathbf{r}_N) \prod_{i=1}^{N} d\mathbf{r}_i = N! / (N-l)! \tag{4.9.10}$$

Thus, the quantity of central importance for constructing the theory of quantum systems is the Slater sum; which can, in principle, be found from the solution of the quantum mechanical N-body problem. Unfortunately, the actual calculation is too involved to be feasible.

4.10. Energy Fluctuation in Canonical Ensemble

In the canonical ensemble, the energy E of a system is not fixed, but varies. On the other hand, the energy of a system in the microcanonical ensemble is almost fixed to a given value. But the thermodynamic properties of a system derived through these two approaches are identical. Thus, these two approaches are consistent.

Let us explain the reason for this equivalence. In the canonical ensemble, the mean energy of the system is given by

$$U \equiv \langle E \rangle = \sum_n E_n g_n \exp(-\beta E_n) / \sum_n g_n \exp(-\beta E_n) \tag{4.10.1}$$

Differentiating it with respect to β, and keeping E_n (hence V) constant, we get

$$\partial U/\partial\beta = -[\sum_n E_n^2 g_n \exp(-\beta E_n) / \sum_n g_n \exp(-\beta E_n)] + [\sum_n E_n g_n \exp(-\beta E_n) / \sum_n g_n \exp(-\beta E_n)]^2$$

$$= -[\langle E^2 \rangle - \langle E \rangle^2] \tag{4.10.2}$$

Then, the relative mean square fluctuation in energy E is

$$\langle (\Delta E)^2 \rangle \equiv \langle E^2 \rangle - \langle E \rangle^2 = -(\partial U/\partial\beta) = kT^2(\partial U/\partial T)$$

$$= kT^2 C_V \tag{4.10.3}$$

where C_V is the specific heat at constant volume. The relative root mean square fluctuation in E is given as

$$\sqrt{[\langle (\Delta E)^2 \rangle]} / \langle E \rangle = \sqrt{(kT^2 C_V)} / U \tag{4.10.4}$$

which is of the order of $O(N^{-1/2})$ (N is the number of particles in the system). For large N, the relative root mean square fluctuation in E is negligible. On neglecting the fluctuation of E, a system in the canonical ensemble has an energy equal to or almost equal to the mean energy U. In this situation the canonical ensemble is equivalent to the microcanonical ensemble, and they will yield practically identical results.

Problems

4.1. Derive Gibbs distribution function and use it to obtain Maxwell distribution law of velocities.

4.2. An ideal gas consisting of N particles is placed in thermal contact with a thermostat at temperature T. Find the probability that the total energy of the gas lies in the interval E and E + dE.

4.3. What do you understand by the canonical partition function. Calculate the partition function for a perfect monatomic gas. Hence obtain its thermodynamic properties.

4.4. Explain Gibbs paradox. How can it be removed. Obtain an expression for the partition function which is free from the Gibbs paradox.

4.5. Show that for an ideal gas the entropy is given by
$S = Nk [\ln (Q_1/N) + T(\partial \ln Q_1 / \partial T)_P]$

4.6. Show that the partition function Q_N of an extreme relativistic gas consisting of N noninteracting molecules with energy-momentum relationship $\epsilon = CP$ (C being the velocity of light) is given by
$Q_N = (1/N!) [8\pi V(kT/hC)^3]^N$
Hence deduce the specific heat of the gas.

4.7. Discuss the partition function of a perfect monotonic gas in a two-dimensional space. Derive expressions for Helmholtz free energy and enthalpy of the two dimensional gas.

4.8. Derive thermodynamic properties of an extreme relativistic gas in a two-dimensional space.

4.9. Explain what do you understand by partition function and phase integral. Show that the partition function of a localised simple harmonic oscillator may be written as
$Q_1 = \exp(-\hbar\omega/2kT) (1 - \exp(-\hbar\omega/kT)^{-1}$

4.10. Calculate the partition function of a system of non-interacting linear anharmonic oscillators. The Hamiltonian of a single anharmonic oscillator is given by
$H(p_x, x) = (p_x^2/2m) + (1/2)m\omega^2x^2 + \alpha x^2 + \beta x^4$
obtain an approximate expression for the specific heat of the system.

4.11. Obtain the specific heat of a system consisting of N noninteracting quantum mechanical linear anharmonic oscillators. The energy levels of a single anharmonic oscillator can be approximated as
$E_n = (n + (1/2))\hbar\omega - a(n + (1/2))^2 (\hbar\omega)^2$
$n = 0, 1, 2, \ldots$ The parameter $a << 1$, and represents the degree of anharmonicity.

4.12. Calculate the partition function of a relativistic ideal gas. Discuss the limiting cases of nonrelativistic and extreme relativistic particles. Calculate the average energy in the extreme relativistic case.

4.13. Consider a system consisting of N_1 molecules of species 1, N_2 molecules of species 2, ..., N_s molecules of species s, such that $N = \sum_{i=1}^{N} N_i$. Show that the partition function of such a system, when the interaction is neglected, is given by
$Q_N = V^N / \prod_{i=1}^{S} N_i! \lambda_i^{3N_i}$
where λ_i is the thermal wavelength of ith species. Calculate the Helmholtz free energy for such a system.

4.14. Calculate the partition function and the thermodynamic properties of an ideal gas consisting of N_1 molecules of mass m_1, and N_2 molecules of mass m_2, enclosed in vessel of volume V at temperature T. Assume that the molecules of a given kind are mutually indistinguishable.

4.15. Compare the results of problem 4.14 with those obtained for an ideal gas consisting of (N_1+N_2) identical molecules of mass m, such that $m = (m_1N_1+m_2N_2)/ (N_1+N_2)$.

CHAPTER 5

GRAND CANONICAL ENSEMBLE

5.1. System with Fixed Chemical Potential

In the previous chapter we studied the canonical ensemble in which the number of particles of the system is fixed, but the energy E is variable. However, there are number of physical as well as chemical systems, which are either exchanging particles with other systems or generating an unlimited number of particles of a definite type. For example, electromagnetic radiation in a container may be treated as a gas of photons, the number of particles of which is not definite, since photons are emitted and absorbed continuously by the walls of container. The system in which both the number of particles N and energy E vary is called an open system. We may consider the system immersed in a heat reservoir with which it may exchange both energy and particles. A large number of mental copies of the given system in thermal contact with a heat reservoir form an ensemble, which is called a grand canonical ensemble. In this case, the distribution function depends not only on the energy of the quantum states but also on the number N of the particles in the system.

In a grand canonical ensemble, both energy E and number N of particles are variable. However, the system in contact with the reservoir forms a composite system whose energy and number of particles are fixed. This composite system is described by the microcanonical ensemble.

5.2. Grand Canonical Distribution

We consider a system A in contact with a heat reservoir B, with which it may exchange both energy and particles (Fig.5.1). Let the system be in equilibrium with the reservoir having a common temperature T. The composite system is a large closed system, which has a constant energy E_0 and constant number of particles N_0. Suppose that at any time the system and the reservoir consist of N_1 and N_2 particles respectively and have energies E_1 and E_2; then

$$N_1 + N_2 = N_0 = \text{Constant}$$

$$E_1 + E_2 = E_0 = \text{Constant}$$

Since the reservoir is supposed to be much larger than the system,

$$N_1 \ll N_2$$

$$E_1 \ll E_2$$

The composite system in this case also is adiabatically isolated. Hence the microcanonical distribution is applied. As result, the probability dW that the system and the reservoir, respectively, are in elements $d\Gamma_1$ and $d\Gamma_2$ is given by

$$dW = C\,\delta(E_1 + E_2 - E_0)\,d\Gamma_1\,d\Gamma_2 \tag{5.2.1}$$

Let us find out the probability ρ_{nN} that the system A is in a definite quantum state with energy E_{nN} (E_{nN} is the energy value of the n^{th} quantum state with the number N of particles). This can be obtained by putting $d\Gamma_1 = 1$, $E_1 = E_{nN}$, and integrating with respect to Γ_2. Thus

$$\rho_{nN} = C \int \delta(E_2 - [E_0 - E_{nN}])d\Gamma_2 \tag{5.2.2}$$

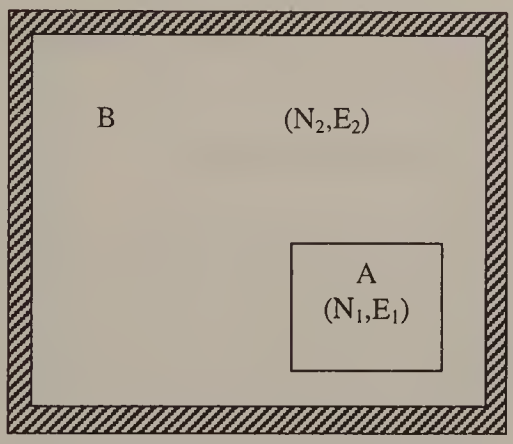


Fig.5.1. A system immersed in a particle energy reservoir in equilibrium

In this case also (as we have obtained in the case of canonical ensemble) $d\Gamma_2$ can be expressed in terms of the entropy of the reservoir. However, in this case the entropy will be a function of its energy E_2 and the number of particles N_2. Thus [see Eq.(4.2.3)]

$$d\Gamma_2 = (\exp(S_2(E_2,N_2)/k)/\Delta E_2)dE_2 \tag{5.2.3}$$

where $S_2(E_2,N_2)$ is the entropy of the reservoir.

Substituting (5.2.3) in (5.2.2) and using the properties of the delta function, we obtain the result as

$$\rho_{nN} = C\,(\exp(S_2(E_0 - E_{nN}, N_0 - N)/k)/\Delta(E_0 - E_{nN})) \tag{5.2.4}$$

Here we have used $N_2 = N_0 - N$.

The variation in ΔE is very small when E varies slightly. So we can write

$$\Delta(E_0 - E_{nN}) = \Delta E_0 = \text{constant}$$

Further, the energy E_{nN} of the system is small in comparison with E_0. We expand S_2 in power of E_{nN} and N as

$$S_2(E_0 - E_{nN}, N_0 - N) = S_2(E_0,N_0) - E_{nN}\,(\partial S_2(E_0,N_0)/\partial E_0)_{N_0} - N(\partial S_2(E_0,N_0)/\partial N_0)_{E_0}$$

$$= S_2(E_0,N_0) - (E_{nN}/T) + (\mu N/T)$$

since

$$(\partial S_2(E_0,N_0)/\partial E_0)_{V,N_0} = 1/T$$

$$(S_2(E_0,N_0)/N_0)_{V,E_0} = -\mu/T$$

Here μ is the chemical potential per particle of the system. Thus we have from (5.2.4)

$$\rho_{nN} = A \exp((\mu N - E_{nN})/kT) \tag{5.2.6}$$

where

$$A = C \exp(S_2(E_0)/k)/\Delta E_0 \tag{5.2.7}$$

is a normalisation constant and is given by the normalisation condition

$$\sum_N \sum_n \rho_{nN} = 1 \tag{5.2.8}$$

Thus

$$\Xi \equiv 1/A = \sum_N \sum_n \exp((\mu N - E_{nN}) / kT) \tag{5.2.9}$$

Equation (5.2.6) is known as Gibb's grand canonical distribution or simply grand canonical distribution for an open system. Ξ is called the grand canonical partition function.
In classical statistics, a similar expression for Gibb's grand canonical distribution function in phase space is

$$\rho_N(q,p) = A \exp((\mu N - E_N(q,p))/kT) \tag{5.2.10}$$

where $E_N(q,p)$ is the energy of the system with a given number N of particles, which is a function of its coordinate q and momentum p. The normalisation constant A is given by the condition

$$\sum_N \int \rho_N(q,p) dq\, dp = 1 \tag{5.2.11}$$

Thus

$$\Xi \equiv 1/A = \sum_N \exp(\mu N)/kT) \int \exp(-E_N(q, p) / kT)\, dq\, dp \tag{5.2.12}$$

where Ξ is the grand canonical partition function in classical statistics. However, the correct way of expressing Ξ is

$$\Xi = \sum_N (\exp(\mu N)/kT)/N!h^{3N}) \int \exp(-E_N(q, p)/kT)\, dq\, dp \tag{5.2.13}$$

where

$$dq\, dp = \prod_{i=1}^{N} dq_i dp_i$$

The corresponding distribution function is

$$\rho_N(q,p) = (1/N!h^{3N}\,\Xi)\exp((\mu N - E_N(q,p))/kT) \tag{5.2.14}$$

The extra factor N! enters in (5.2.13) because there are N! ways of assigning the indistinguishable particles.

Comparing with the expression of the canonical partition function, we can write Ξ as

$$\Xi(z', V, T) = \sum_{i=1}^{\infty} z'^N Q_N \tag{5.2.15}$$

where

$$z' = e^{\mu/kT} \tag{5.2.16}$$

5.3. Thermodynamic Functions for the Grand Canonical Ensemble

In this case, the entropy is fixed by the energy and number of particles of the system. As we have discussed in canonical ensemble, the entropy of the system of the grand canonical ensemble with mean energy <E> and mean number <N> of particles will be equal to the entropy of the microcanonical ensemble with <E> and <N>. Then, by definition, the entropy is given by

$$S = k \ln \Delta\Gamma = -k \ln \rho\,(\langle E\rangle, \langle N\rangle) \tag{5.3.1}$$

According to the grand canonical distribution, we have

$$\rho(\langle E\rangle,\langle N\rangle) \equiv \rho_{\langle N\rangle}(\langle E\rangle) = e^{(\mu\langle N\rangle-\langle E\rangle)/kT}/\Xi \tag{5.3.2}$$

Substituting this value, (5.3.1) can be written as

$$S = k \ln \Xi - (\mu\langle N\rangle/T) + (\langle E\rangle/T)$$

or

$$\langle E\rangle - ST - \mu\langle N\rangle = -kT \ln \Xi \tag{5.3.3}$$

Here $\langle E\rangle = U$ is the internal energy. But $A = U - ST$ is the free energy

$$\Omega = A - \mu\langle N\rangle$$

is the thermodynamic potential, which depends on T, V and μ, and is often called the grand canonical potential because of its relation to the grand canonical partition. Thus,

$$\Omega = -kT \ln \Xi \tag{5.3.4}$$

The Gibb's free energy is defined as

$$G = U - ST + PV$$

$$= A + PV \tag{5.3.5}$$

On differentiation (5.3.5) yields

$$dG = dA + PdV + VdP$$

But

$$dA = -SdT - PdV + \mu dN$$

Then, we get

$$dG = -SdT + VdP + \mu dN \tag{5.3.6}$$

This gives

$$(\partial G/\partial N)_{P,T} = \mu$$

Hence for fixed P and T

$$G = \mu N \tag{5.3.7}$$

In this case N is replaced by <N>. Then, it can be shown that

$$\Omega(T, V, \mu) = -PV \tag{5.3.8}$$

From (5.3.4) and (5.3.8), we get

$$PV/kT = \ln \Xi \tag{5.3.9}$$

This provides a link between thermodynamics and Ξ. Further differentiating the grand potential $\Omega = A - \mu\langle N\rangle$, we have

$$\begin{aligned} d\Omega &= dA - \mu d\langle N\rangle - \langle N\rangle d\mu \\ &= -PdV - SdT - \langle N\rangle d\mu \end{aligned} \tag{5.3.10}$$

which gives

$$P = -(\partial\Omega/\partial V)_{S,\mu} = kT(\partial \ln \Xi / \partial V)_{S,\mu} \tag{5.3.11a}$$

$$S = -(\partial\Omega/\partial T)_{V,\mu} = k(\partial (T \ln \Xi)/\partial V)_{V,\mu} \tag{5.3.11b}$$

$$\langle N\rangle = -(\partial\Omega/\partial\mu)_{V,T} = kT(\partial \ln \Xi / \partial\mu)_{V,T} \tag{5.3.11c}$$

From these relations, we can calculate the thermodynamic properties for the grand canonical ensemble. Thus, the Helmholtz free energy is given by

$$A = +\mu\langle N\rangle + \Omega = NkT \ln z' - kT \ln \Xi = -kT \ln (\Xi/z'^N) \tag{5.3.12}$$

which may be compared with the canonical ensemble formula $A = - kT \ln Q_N$. Finally, we have for the internal energy of the system

$$\begin{aligned} U &= A + ST \\ &= NkT \ln z' - kT \ln \Xi + kT \ln (\partial(T \ln \Xi)/\partial T)_{V,\mu} \\ &= NkT \ln z' + kT^2 (\partial \ln \Xi / \partial T)_{V,\mu} \\ &= kT^2 (\partial \ln \Xi / \partial T)_{z',V} \end{aligned} \tag{5.3.13}$$

Since

$$\begin{aligned} (\partial \ln \Xi / \partial T)_{\mu,V} &= (\partial \ln \Xi / \partial T)_{z',V} + (\partial \ln \Xi / \partial \ln z')_{T,V} (\partial \ln z' / \partial T)_{\mu,V} \\ &= (\partial \ln \Xi / \partial T)_{z',V} - (N/T) \ln z' \end{aligned} \tag{5.3.14}$$

5.4. Classical System in the Grand Canonical Ensemble

Let us consider an open classical system of identical particles, each of mass m in thermal equilibrium at a temperature T. The Hamiltonian of the system of N identical particles is given by

$$H_N(q, p) = \sum_{i=1}^{N} (p_i^2/m) + U(r_1, r_2, \ldots r_N) \tag{5.4.1}$$

where U is the interaction potential.
The grand canonical partition function for this system can be written as

$$\Xi = \sum_{N=0} (e^{\mu N/kT}/N!h^{3N}) \int\int \exp(-H_N(q,p)/kT) \prod_{i=1}^{N} d\mathbf{p}_i d\mathbf{r}_i \tag{5.4.2}$$

Substituting (5.4.1) in (5.4.2), and after momentum integration, we get

$$\Xi = \sum_{N=0}^{\infty} (e^{\mu N/kT}/N!\lambda^{3N}) \int\int e^{-U/kT} \prod_{i=1}^{N} d\mathbf{r}_i \tag{5.4.3}$$

where λ is the thermal wavelength. If we introduce the fugacity, defined by

$$z = e^{\mu/kT}/\lambda^3 = z'/\lambda^3$$

(in the literature z' is often referred to as fugacity), then (5.4.3) can be written as

$$\Xi(z, V, T) = \sum_{N=0}^{\infty} z^N Z_N/N! \tag{5.4.4}$$

where

$$Z_N = \int\int e^{-U/kT} \prod_{i=1}^{N} d\mathbf{r}_i \tag{5.4.5}$$

is the configurational integral of the system (with $Z_0 = 1$). For an ideal gas of non-interacting system, (5.4.5) reduces to

$$Z_N^{id} = V^N$$

and

$$\Xi^{id}(z, V, T) = \sum_{N=0}^{\infty} z^N V^N/N! \tag{5.4.6}$$

$$= e^{zV} \tag{5.4.7}$$

This expression can be used to calculate the thermodynamic properties in the grand canonical ensemble. Thus, we have for an ideal gas

$$\Omega^{id} = -kT \ln \Xi^{id} = -kT\, zV \tag{5.4.8}$$

$$\langle N \rangle = -(\partial\Omega^{id}/\partial\mu)_{V,T} = zV \tag{5.4.9}$$

Using the relation

$$P = -(kT/V) \ln \Xi$$

the pressure is

$$P = kTz = \langle N \rangle kT/V \tag{5.4.10}$$

Similarly, the l-particle density distribution function in the grand canonical ensemble can be given by

$$n(r_1, r_2, \ldots r_l) = \sum_{N \geq l} (N!/(N-l)!) \int\int \rho_N(r^N, p^N)\, d\mathbf{p}^N\, d\mathbf{r}^{N-l}$$

$$= \Xi^{-1} \sum_{N \geq l} (e^{\mu N/kT}/(N-l)!h^{3N}) \int \exp(-H_N(q,p)/kT)\, d\mathbf{p}^N d\mathbf{r}^{N-l} \tag{5.4.11}$$

where $H_N(q,p)$ is the Hamiltonian of the system. Substituting (5.4.1) in (5.4.11) and integrating over momenta, we get

$$n(r_1, r_2, \ldots r_l) = \Xi^{-1} \sum_{N \geq l} (z^N/(N-l)! \int e^{-U/kT}\, d\mathbf{r}^{N-l} \tag{5.4.12}$$

It can also be written in the form

$$n(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_l) = \Xi^{-1} \sum_{N \geq l} (z^N Z_N\, n_N(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_l)/N! \tag{5.4.13}$$

where n_N is the l-particle distribution function in the canonical ensemble.

The normalisation equation for $n(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_l)$ is

$$\int\int n(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_l) \prod_{i=1}^{N} d\mathbf{r}_i = \Xi^{-1} \sum_{N\geq l} (z^N Z_N/(N-l)!)$$

$$= \sum_{N\geq l} (N!/(N-l)!)P_N = < N!/(N-l)!>$$

$$= <N^l - (l(l-1)/2)N^{l-1} + \ldots >$$

$$= <N^l [1 - (l(l-1)/2)(1/N) + \ldots]>$$

$$= <N^l> [1 - ((l-1)/2)(1/<N>) + \ldots]$$

$$= <N^l> [1 - 0(1/N)] \qquad (5.4.14)$$

Here we have used a quantity

$$P_N = z^N Z_N/N!\,\Xi \qquad (5.4.15)$$

which is the probability that an open system contains N molecules. In the limit $V \to \infty$, $N \to \infty$ (z and T are fixed), $<N^l> = <N>^l$, and hence

$$\lim_{V\to\infty} (1/V^l \rho^l \int n(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_l) \prod_{i=1}^{N} d\mathbf{r}_i = 1 \qquad (5.4.16)$$

where $\rho = N/V$. This is the normalisation condiion used by Mayer (1942).

5.5. Quantum System in the Grand Canonical Ensemble

In this section, we consider an open quantum system of identical particles, each of mass m at a temperature T. The Hamiltonian operator of the system of N identical particles

$$\hat{H}_N = -(\hbar^2/2m) \sum_{i=1}^{N} \nabla_i^2 + U(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N) \qquad (5.5.1)$$

The statistical operator $\hat{\rho}$ for an open system is defined as

$$\hat{\rho} = \exp [-(\hat{H}_N - \mu\hat{N}) / kT] / \Xi \qquad (5.5.2)$$

where $\hat{N}$ is a number operator, whose eigen values are 0, 1, 2, ... Using the normalization condition

$$\sum_N \sum_n = \rho_{nN} = 1 \qquad (5.5.3)$$

the grand canonical partition function for the quantum system can be written as

$$\Xi = \sum_{N=0}^{\infty} \sum_n \int\int \Psi_{nN}^* \exp((\mu\hat{N} - \hat{H}_N)/kT) \Psi_{nN} \prod_{i=1}^{N} d\mathbf{r}_i \qquad (5.5.4)$$

where $\Psi_{nN}(\mathbf{r}_1, ..., \mathbf{r}_N)$ is a complete set of (properly symmetrised) orthogonal wave functions of the system of N particles.

In terms of Slater sum, defined by

$$W_N(\mathbf{r}_1, ..., \mathbf{r}_N) = N!\,\lambda^{3N} \sum_n \Psi^*_{nN}(\mathbf{r}_1, \mathbf{r}_2, ... \mathbf{r}_N) \exp(-\hat{H}_N/kT)\, \Psi_{nN}(\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_N)$$

$$= N!\,\lambda^{3N} < \mathbf{r}_1, ..., \mathbf{r}_N | \exp(-\hat{H}_N/kT) | \mathbf{r}_1, ..., \mathbf{r}_N > \qquad (5.5.5)$$

the grand canonical partition function can be written as

$$\Xi = \sum_{N=0}^{\infty} (z^N/N!) \int ... \int W_N(\mathbf{r}_1,\mathbf{r}_2,..., \mathbf{r}_N) \prod_{i=1}^{N} d\mathbf{r}_i \qquad (5.5.6)$$

$$= \sum_{N=0} z^N Z_N/N! \qquad (5.5.7)$$

where

$$Z_N = \int ... \int W_N(\mathbf{r}_1,\mathbf{r}_2,..., \mathbf{r}_N) \prod_{i=1}^{N} d\mathbf{r}_i \qquad (5.5.8)$$

$$z = e^{\mu/kT}/\lambda^{3N}$$

is the fugacity for the quantum system.

Similarly, the l-particle density distribution function in the grand canonical ensemble is

$$n(\mathbf{r}_1, \mathbf{r}_2, ... \mathbf{r}_l) = \Xi^{-1} \sum_{N \geq l} (z^N/(N-l)! \int ... \int W_N(\mathbf{r}_1,\mathbf{r}_2,..., \mathbf{r}_N) \prod_{i=l}^{N} d\mathbf{r}_i \qquad (5.5.9)$$

The normalisation of $n(\mathbf{r}_1, \mathbf{r}_2, ... \mathbf{r}_l)$ is again given by

$$\int\int n(\mathbf{r}_1, \mathbf{r}_2, ... \mathbf{r}_l) \prod_{i=1}^{N} d\mathbf{r}_i = \Xi^{-1} \sum_{N \geq l} (z^N Z_N/(N-l)! \qquad (5.5.10)$$

5.6. Density and Energy Fluctuations in the Grand Canonical Ensemble

In a grand canonical ensemble, the variables N and E of the system are not fixed, but vary. However, the thermodynamic properties are obtained against their mean values <N> and <E>. The basic reason for this is related to the fact that the relative fluctuations of these quantities are negligible. This point can be appreciated by calculating the relative fluctuations in the density $\rho(\equiv N/V)$, and the energy E of a given system in the grand canonical ensemble.

In this ensemble the mean number of particles is given by

$$<N> = \sum_N \sum_n N \exp(\beta(\mu N - E_{nN})) / \sum_N \sum_n \exp(\beta(\mu N - E_{nN})) \qquad (5.6.1)$$

Differentiating it with respect to μ, and keeping the energy value E_{nN} constant, we obtain

$$(\partial\langle N\rangle/\partial\mu)_{V,T} = \beta\,[\underset{N\,n}{\Sigma\Sigma} N^2 \exp(\beta(\mu N - E_{nN})) \,/\, \underset{N\,n}{\Sigma\Sigma}\exp(\beta(\mu N - E_{nN}))$$

$$- \{\underset{N\,n}{\Sigma\Sigma} N \exp(\beta(\mu N - E_{nN})) \,/\, \underset{N\,n}{\Sigma\Sigma}\exp(\beta(\mu N - E_{nN}))\}^2\,]$$

$$= \beta\,[\langle N^2\rangle - \langle N\rangle^2] = \beta\,\langle(\Delta N)^2\rangle \qquad (5.6.2)$$

The relative mean square fluctuation in the particle density ρ is then

$$\langle(\Delta\rho)^2\rangle / \langle\rho\rangle^2 \equiv (\langle\rho^2\rangle - \langle\rho\rangle^2)/\langle\rho\rangle^2$$

$$= \langle(\Delta N)^2\rangle / \langle N\rangle^2 = (kT/N^2)\,(\partial N/\partial\mu)_{V,T} \qquad (5.6.3)$$

where $\langle N\rangle$ is replaced by N in the last expression. Now, from the thermodynamic relation, we have for T constant.

$$d\mu = \nu dP \qquad (5.6.4)$$

where $\nu = V/N$; therefore

$$(\partial\mu/\partial\nu)_T = \nu\,(\partial P/\partial V)_T \qquad (5.6.5)$$

or

$$-(N^2/V)(\partial\mu/\partial N)_{V,T} = V(\partial P/\partial V)_{N,T} \qquad (5.6.6)$$

substituting this value in (5.6.3), we get

$$\langle(\Delta\rho)^2\rangle/\langle\rho\rangle^2 \equiv (\langle\rho^2\rangle-\langle\rho\rangle^2)/\langle\rho\rangle^2 = -(kT/V^2)\,(\partial V/\partial P)_{N,T}$$

$$= (kT/V)K_T \qquad (5.6.7)$$

where

$$K_T = -(1/V)\,(\partial V/\partial P)_{N,T}$$

is the isothermal compressibility of the system.

The relative root mean square fluctuation in particle density of the given system is $O(N^{-1/2})$, which is negligible when N is very large ($N\sim10^{23}$). On neglecting the fluctuation of the number N, we obtain $\Omega+\mu\langle N\rangle = A$. Then the grand canonical distribution becomes identical with the canonical distribution. Then we must have

$$\Xi(z', V, T) = z'^N Q_N(V,T) \qquad (5.6.8)$$

However, there are some exceptions like phase transitions, or critical region, where the fluctuations become very large. In such cases, the formalism of the grand canonical ensemble will provide a correct picture of the physical situation, and will be preferred.

Let us now examine the fluctuation in the energy of the system. The mean energy <E> of the system is given by

$$U \equiv \langle E \rangle = \sum_N \sum_n E_{nN} \exp(\beta(\mu N - E_{nN})) \Big/ \sum_N \sum_n \exp(\beta(\mu N - E_{nN})) \tag{5.6.9}$$

Differentiating it with respect to β, and keeping E_{nN} and z as constants, we get

$$\partial U/\partial\beta = -\{ \sum_N \sum_n E_{nN}^2 \exp(\beta(\mu N - E_{nN})) \Big/ \sum_N \sum_n \exp(\beta(\mu N - E_{nN})) \}$$

$$+ \{ \sum_N \sum_n E_{nN} \exp(\beta(\mu N - E_{nN})) \Big/ \sum_N \sum_n \exp(\beta(\mu N - E_{nN})) \}^2$$

$$= -[\langle E^2 \rangle - \langle E \rangle^2] = -\langle (\Delta E)^2 \rangle \tag{5.6.10}$$

or

$$\langle (\Delta E)^2 \rangle = -(\partial U/\partial\beta)_{z,V} = kT^2 (\partial U/\partial T)_{z,V} \tag{5.6.11}$$

Hence the relative mean square fluctuation in E is

$$\langle (\Delta E)^2 \rangle / \langle E \rangle^2 = (kT^2/U^2)(\partial U/\partial T)_{z,V} \tag{5.6.12}$$

Let us first write

$$(\partial U/\partial T)_{z,V} = (\partial U/\partial T)_{N,V} + (\partial U/\partial N)_{V,T} (\partial N/\partial T)_{z,V} \tag{5.6.13}$$

and

$$(\partial N/\partial T)_{z,V} = (\partial N/\partial T)_{\mu,V} + (\partial N/\partial \mu)_{T,V} (\partial \mu/\partial T)_{z,V}$$

$$= -(\partial N/\partial \mu)_{T,V} (\partial \mu/\partial T)_{N,V} + (\partial N/\partial \mu)_{T,V} (\mu/T)$$

$$= (1/T)(\partial N/\partial \mu)_{T,V} [\mu - T(\partial \mu/\partial T)_{N,V}]$$

$$= (1/T)(\partial N/\partial \mu)_{T,V} (\partial U/\partial N)_{T,V} \tag{5.6.14}$$

since

$$(\partial U/\partial N)_{T,V} = \mu - T(\partial \mu/\partial T)_{N,V}$$

Substituting (5.6.13) and (5.6.14) in (5.6.11), we finally obtain

$$\langle (\Delta E)^2 \rangle = kT^2 (\partial U/\partial T)_{N,V} + kT (\partial N/\partial \mu)_{T,V} [(\partial U/\partial N)_{T,V}]^2$$

$$= kT^2 C_V + \langle (\Delta N)^2 \rangle [(\partial U/\partial N)_{T,V}]^2 \tag{5.6.15}$$

where C_V is the specific heat at constant volume. But

$$\langle (\Delta E)^2 \rangle_{can} = kT^2 C_V \tag{5.6.15}$$

is the mean square fluctuation in the energy E of a system in the canonical ensemble. Thus we seen that the mean square fluctuation in the energy of a given system is equal to $\langle (\Delta E)^2 \rangle_{can}$ plus a term

arising due to the fluctuation of the particle number N. Generally, the relative root mean square fluctuation in the energy of the system is practically negligible. On neglecting the fluctuations in E and N, a system in the grand canonical ensemble has an energy and particle number equal to the mean energy U and mean particle number <N>. In this case, the grand canonical ensemble is equivalent to the microcanonical ensemble.

5.7. Thermodynamic Equivalence of Ensembles

So far, we have discussed closed isolated systems (microcanonical ensemble), closed isothermal systems (canonical ensemble), and open isothermal systems (grand canonical ensemble). We have seen that both canonical and grand canonical ensembles can be deduced from the microcanonical ensemble.

In the microcanonical ensemble, the energy E and particle number N are fixed. Thus it neglects the fluctuation in E and N, while the canonical ensemble takes into account the fluctuation in E but neglects the fluctuation in N. On the other hand, the grand canonical ensemble takes into account both these fluctuations and may be said to be canonical with respect to both energy and the particle number. The grand canonical ensemble may be viewed as a collection of canonical ensembles of different number of particles, while the canonical ensemble is a collection of microcanonical ensembles of different energies.

These three distribution give identical results for the thermodynamic functions at mean energy <E> and mean particle number <N>. However, in the thermodynamic limit, the grand canonical ensemble is the most convenient and is commonly used, while the microcanonical ensemble is the most inconvenient.

Problems

5.1 Derive the grand partition function. Show that the equation of state of a system is given by

$$PV = kT \ln \Xi$$

5.2 Show that the grand partition function is given by

$$\Xi = \sum_{N=0}^{\infty} z^N Q_N$$

where Q_N is the canonical partition function.

5.3 Calculate the grand partition function for an ideal gas and hence obtain the equation of state for the ideal gas.

5.4 Derive the grand partition function for an ideal gas in a two-dimensional space and compare it with that for an ideal gas in a three-dimensional space.

5.5 Consider a binary mixture consisting of N_1 molecules of species 1, and N_2 molecules of species 2, such that $N = N_1+N_2$. Derive thermodynamic properties for such a mixture.

5.6 Consider a classical system of N noninteracting harmonic oscillators enclosed in a box of volume V at temperature T. The Hamiltonian of a single harmonic oscillator is given by

$H(p_x, x) = (p_x^2/2m) + (1/2)m\omega^2x^2$

Discuss the thermodynamics of this system.

5.7 Prove that for a system in the grand canonical ensemble

(a) $\langle\rho^2\rangle - \langle\rho\rangle^2 = (kT/V)\langle\rho\rangle^2 K_T$

(b) $\langle(\Delta E)^2\rangle = kT^2C_V + \langle(\Delta N)^2\rangle [(\partial U/\partial N)_{T,V}]^2$

where K_T is the isothermal compressibility.

CHAPTER 6

THEORY OF IDEAL GASES

6.1. The Ideal Gases

Let us consider a system of an ideal gas of identical particles. By an ideal gas we mean a gas in which the interaction between the particles is negligible, so the energy of the system is the sum of the kinetic energy of each particle. When a gas is rarefied, the particles of the gas are far apart and the interaction between them is negligible. This is possible when the pressure of the gas is very low and/or temperature is very high. When the particles of the system obey the classical laws, the system is known as the classical system. On the other hand if the particles of the system obey the quantum laws the system is called the quantum system. In this chapter, we consider both the classical and quantum gases in ideal situation.

A system may be of three types :

(i) Boltzmann system : The particles of the system are distinguishable from one another.

(ii) Bose- Einstein system : The particles of the system are indistinguishable. The total wave function of the system is symmetric under exchange of coordinates of any two particles.

(iii) Fermi-Dirac system : The particles of the system are indistinguishable. The total wave function of the system is antisymmetric under exchange of coordinates of any two particles.

The Bose-Einstein and Fermi-Dirac systems are the quantum system, while the Boltzmann system is the classical one.

6.2. System of Indistinguishable Particles

Let us consider a system of N noninteracting particles. The Hamiltonian of the system is simply a sum of the single particle Hamiltonian.

$$\hat{H}_N(q, p) = \sum_{i=1}^{N} \hat{H}_i(q_i, p_i) \tag{6.2.1}$$

where $\hat{H}_i(q_i, p_i)$ is the Hamiltonian of the ith particle. Let $\Psi_N(q)$ be a complete wave function of the system, which can be written as

$$\Psi_N(q) = \prod_{i=1}^{N} \phi_i(q_i) \tag{6.2.2}$$

$\phi_i(q_i)$ being the state occupied by the ith particle. Thus

$$\hat{H}_i(q_i, p_i)\, \phi_i(q_i) = \epsilon_i \phi_i(q_i) \tag{6.2.3}$$

where ϵ_i is the eigenvalue corresponding to the eigenstate $\phi_i(q_i)$. In general there are n_i particles occupying the states with energy ϵ_i. Clearly, the possible value of n_i will be governed by the conditions that the total number of particles N and the total energy E are given by

$$\sum_i n_i = N \tag{6.2.4}$$

$$\sum_i n_i \epsilon_i = E \tag{6.2.5}$$

Accordingly the wave function of this state may be given by

$$\Psi_N(q) = \prod_i \prod_{j=1}^{n_i} \phi_i(q_j) \tag{6.2.6}$$

Let P_{jk} be the permutation operator, which interchanges the coordinates q_j and q_k. Then,

$$P_{jk}\Psi_N(q) \equiv P_{jk}\Psi_N(q_1, \ldots q_j, q_k, \ldots, q_N)$$

$$= \Psi'_N(q_1, \ldots q_k, q_j, \ldots, q_N) \tag{6.2.7}$$

Unless $\phi_i(q_j) = \phi_i(q_k)$, Ψ'_N will be a wave function distinct from Ψ_N. This is only possible when the (identical) particles of the system are regarded as distinguishable. The statistics governing the behaviour of the system characterised by such type of wave function is called Maxwell-Boltzmann or simply, Boltzmann statistics.

In quantum statistics, where particles of the system are indistinguishable, we have the following two possibilities

$$P_{jk}\Psi_N = \Psi_N \tag{6.2.8}$$

which means that the wave function is symmetric in its arguments or

$$P_{jk}\Psi_N = -\Psi_N \tag{6.2.9}$$

which means that wave function is antisymmetric in its arguments. We call these wave functions Ψ_S and Ψ_A, respectively. Let us call the wave function of the type (6.2.6) as Boltzmann function denoted by Ψ_B, then Ψ_S and Ψ_A for a system of N identical particles are given by

$$\Psi_S(q) = a \sum_P P\,\Psi_B(q) \tag{6.2.10}$$

$$\Psi_A(q) = a \sum_P \delta_P P \Psi_B(q) \tag{6.2.11}$$

where $\delta_P = +1$ if P is even

$= -1$ if P is odd.

and a is constant.

The statistics governing the behaviour of the system characterised by the symmetric wave functions, is called Bose- Einstein, or simply Bose statistics. Particles forming the Bose system are called bosons.

The statistics governing the behaviour of the system, which is characterised by the antisymmetric wave functions, is called Fermi- Dirac or simply, Fermi statistics. Particles forming a Fermi system are called fermions. The function $\Psi_A(q)$ can be expressed in the form of a Slater determinant

$$\Psi_A(q) = a \begin{vmatrix} \phi_1(q_1) & \phi_1(q_2), \ldots, \phi_1(q_N) \\ \phi_2(q_1) & \phi_2(q_2), \ldots, \phi_2(q_N) \\ \ldots & \ldots \quad \ldots \\ \phi_N(q_1) & \phi_N(q_2), \ldots, \phi_N(q_N) \end{vmatrix} \tag{6.2.12}$$

If two or more particles will be in the same single-particle state, the corresponding row of the determinant will be equal and the wave function will vanish identically. So there is no wave function for the Fermi system with two particles in the same state. This is in accordance with Pauli's exclusion principle. Thus a system of particles obeying the exclusion principle, must be governed by Fermi-Dirac statistics.

Lastly, let us point out that the statistics governing a system is connected with the spin of its particles. Particles having an integral spin (in unit of $\hbar$) obey Bose-Einstein statistics, while particles having a half odd integral spin obey Fermi-Dirac statistics. For example, photons, phonons, He^4, etc. are bosons while electrons, nucleons, He^3, etc. are fermions.

6.3. Ideal Quantum Gas

We consider a system of N indistinguishable, noninteracting particles confined in a volume V at a temperature T. The Slater sum for such a system is given by

$$W_N(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N) = N! \lambda^{3N} \sum_n \Psi_n^*(\mathbf{r}_1, \ldots \mathbf{r}_N) \exp(-\beta \hat{H}_N) \Psi_n(\mathbf{r}_1, \ldots, \mathbf{r}_N) \tag{6.3.1}$$

where $\hat{H}_N$ is the Hamiltonian of the system

$$\hat{H}_N = -(\hbar^2/2m) \sum_{i=1}^{N} \nabla_i^2 \tag{6.3.2}$$

and Ψ_n is the eigenfunction of the Hamiltonian. In this case U = 0 and the eigenfunctions Ψ_n are the free-particle wave function Ψ_K, described by

$$\begin{aligned} \Psi_K(1, 2, \ldots N) &\equiv \Psi_K(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N) \\ &= (1/\sqrt{N!}) \sum_P \delta_P \{\phi_{k_1}(P1), \ldots, \phi_{k_N}(PN)\} \\ &= (1/\sqrt{N!}) \sum_P \delta_P \{\phi_{Pk_1}(1), \ldots, \phi_{Pk_N}(N)\} \end{aligned} \tag{6.3.3}$$

where

$\delta_P = 1$ for bosons

$$\delta_P = +1 \qquad \text{(P even)}$$

$$= -1 \qquad \text{(P odd) for fermions} \tag{6.3.4}$$

The eigenvalues are given by

$$\hat{H}\Psi_K = E\Psi_K \tag{6.3.5}$$

where

$$E = (\hbar^2K^2/2m) = (\hbar^2/2m)(K_1^2 + K_2^2 + \ldots + K_N^2) \tag{6.3.6}$$

Here $K_i (i = 1, 2, \ldots, N)$ is the wave vector of the individual particle i.

Imposing the periodic boundary conditions, the normalised single particle wave function is given by

$$\Psi_K(\mathbf{r}) = (1/\sqrt{V}) \exp(i\mathbf{K}.\mathbf{r}) \tag{6.3.7}$$

with

$$\mathbf{K} = 2\pi\hat{\mathbf{n}}/V^{1/3} \tag{6.3.8}$$

in which $\hat{\mathbf{n}}$ is a vector, whose components are $\hat{n} = 0, \pm1, \pm2, \ldots$

Substituting (6.3.3) in (6.3.1), we get

$$W_N(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N) = \lambda^{3N} \sum_k \exp(-\beta\hbar^2K^2/2m) [\sum_P \delta_P \{\phi^*_{k_1}(P1), \ldots, \phi^*_{k_N}(PN)\}$$

$$\sum_{P'} \delta_{P'} \{\phi_{k_1}(P'1), \ldots, \phi_{k_N}(P'N)\}] \tag{6.3.9}$$

where P and P' are any of the N! possible permutations. Every term of the sum $\sum_{P'}$ will make the same contributions towards the sum because they differ from one another only in the ordering of the $\mathbf{K}$'s. Therefore, the total contribution of the sum of $\sum_{P'}$ must be (N!) times the contribution of one of these permutations. Further, the summation over $\mathbf{K}$ is equivalent to (1/N!) times a summation over all the vectors $\mathbf{K}_1, \ldots, \mathbf{K}_N$ independently of one another. This factor will cancel the previous factor (N!). Thus the result is

$$W_N(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N) = \lambda^{3N} \sum_{K_1, \ldots, K_N} \exp(-\beta\hbar^2(K_1^2 + K_2^2 + \ldots + K_N^2)/2m)$$

$$[\sum_P \delta_P \{\phi^*_{k_1}(P1)\phi_{k_1}(1)\} \ldots \{\phi^*_{k_N}(PN)\phi_{k_N}(N)\}] \tag{6.3.10}$$

In the limit $V \to \infty$, the summation over $\mathbf{K}_i$ may be replaced by an integration over $\mathbf{K}_i$ according to

$$\sum_{K_i} \to (V/(2\pi)^3) \int d\mathbf{K}_i \tag{6.3.11}$$

Then, (6.3.10) becomes

$$W_N(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N) = (\lambda^{3N}/(2\pi)^{3N}) \sum_P \delta_P [\int \exp(-\beta(\hbar^2K_1^2/2m) + i\mathbf{K}_1.(\mathbf{r}_1 - P\mathbf{r}_1))d\mathbf{K}_1$$

$$\ldots \int \exp\left(-\beta(\hbar^2 K_N^2/2m) + i\mathbf{K}_N.(\mathbf{r}_N - P\mathbf{r}_N)\right) d\mathbf{K}_N \Big]$$

$$= \sum_P \delta_P \left[f(\mathbf{r}_1 - P\mathbf{r}_1) \ldots f(\mathbf{r}_N - P\mathbf{r}_N)\right] \tag{6.3.12}$$

where

$$f(r) \equiv \{\int d\mathbf{K} \exp(-\beta(\hbar^2 K^2/2m) + i\mathbf{K}.\mathbf{r})\} / \{\int d\mathbf{K} \exp(-\beta(\hbar^2 K^2/2m))\} \tag{6.3.13}$$

In order to evaluate (6.3.13), we use the spherical polar coordinates (K, θ, φ). Then integrating on θ and φ, one of the integrals can be written as

$$A \equiv \int d\mathbf{K} \exp\left(-\beta(\hbar^2 K^2/2m) + i\mathbf{K}.\mathbf{r}\right)$$

$$= 2\pi \int_0^\infty dK\, K^2 \exp(-\beta\hbar^2 K^2/2m) \int_0^\pi \exp(iKr\cos\theta) \sin\theta\, d\theta$$

$$= (4\pi/r) \int_0^\infty dK\, K \exp(-\beta\hbar^2 K^2/2m) \sin(Kr)$$

since

$$\int_0^\pi \exp(iKr\cos\theta) \sin\theta\, d\theta = (2/Kr) \sin(Kr)$$

After integrating over K, we get

$$A = (2\pi m/\beta\hbar^2)^{3/2} \exp(-\pi r^2/\lambda^2)$$

The second integral is evaluated as

$$B = \int dK \exp(-\beta\hbar^2 K^2/2m) = 4\pi \int_0^\infty dK\, K^2 \exp(-\beta\hbar^2 K^2/2m)$$

$$= (2\pi m/\beta\hbar^2)^{3/2}$$

Then the final result is

$$f(r) = \exp(-\pi r^2/\lambda^2) \tag{6.3.14}$$

where $r \equiv |\mathbf{r}|$ and λ is the thermal wavelength. Equation (6.3.14) is an exact result for the Boltzmann factor. The sum $\sum_P$ of Eq.(6.3.12) contains N! terms. We may expand the sum $\sum_P$ in the number of permutations between particles. The term corresponding to the unit permutation for which $P\mathbf{r}_i = \mathbf{r}_i$, is $f(0) = 1$. The term corresponding to a permutation which only interchanges the coordinates $\mathbf{r}_i$ and $\mathbf{r}_j$, is $f^2(r_{ij})$ and so on. Thus we can write

$$W_1(1) = 1 \tag{6.3.15a}$$

$$W_2(1,2) = 1 \pm f_{ij}^2 \tag{6.3.15b}$$

$$W_3(1,2,3) = 1 \pm f_{12}^2 \pm f_{13}^2 \pm f_{23}^2 + f_{12} f_{13} f_{23} \tag{6.3.15c}$$

$$W_N(1,2, ..., N) = 1 \pm \sum_{i<j} f_{ij}^2 + \sum_{i<j<k} f_{ij} f_{jk} f_{ik} + ... \tag{6.3.15d}$$

where $f_{ij} \equiv f(\mathbf{r}_i - \mathbf{r}_j)$. The '+' and '-' signs in this expansion correspond to the bosons and fermions, respectively. It is clear from (16.3.14) that f_{ij} vanishes rapidly as $r_{ij} >> \lambda$. It then follows that when the temperature is so high that the thermal wavelength λ is much smaller than the mean interparticle distance $a = (6/\pi\rho)^{1/3}$ ($\rho = N/V$ is the number density), (6.3.15d) reduces to

$$W_3(1,2, ..., N) = 1 \tag{6.3.16}$$

$$Q_N(V,T) = (1/N!\lambda^{3N}) \int\int \prod_{i=1}^{N} d\mathbf{r}_i = V^N/N!\,\lambda^{3N} \tag{6.3.17}$$

This is precisely the result for the ideal classical gas.

Let us now investigate the first quantum correction for an ideal gas at high temperature where the quantum effect is small but not negligible. In this case, we can approximate (6.13.15d) as

$$W_3(1,2, ..., N) \quad 1 \pm \sum_{i<j} f_{ij}^2 \quad \prod_{i<j} [1 + f_{ij}]^2$$

$$= \exp(-\beta \sum_{i\leq j} \tilde{u}_{ij}) \tag{6.3.18}$$

where

$$\tilde{u}_{ij} = -kT \ln [1 \pm f_{ij}^2] = -kT \ln [1 \pm \exp(-2\pi r_{ij}^2/\lambda^2)] \tag{6.3.19}$$

Then the partition function in this case becomes

$$Q_N(V,T) = (1/N!\lambda^{3N}) \int\int \exp(-\beta \sum_{i<j} \tilde{u}_{ij}) \prod_{i=1}^{N} d\mathbf{r}_i \tag{6.3.20}$$

This shows that the quantum correction to the partition function of an ideal gas appears in the form of so-called statistical potential $\tilde{u}_{ij}$, which is demonstrated in Fig.6.1 for a pair of particles obeying Bose Einstein and Fermi-Dirac statistics. The potential is attractive for bosons, and repulsive for fermions. In this sense, it gives rise to the 'statistical attraction' between bosons, and the 'statistical repulsion' between fermions. It is however clear that this potential arises only due to the symmetry property of the wave functions and vanishes rapidly as r becomes larger than λ. Thus its effect becomes less important as the temperature of the system increases.

6.4. The Ideal Gases in Microcanonical Ensemble

In this section, we derive the various statistics, discussed in the section 6.1 for an ideal gas. The derivation is based on a method in which the entropy of a gas in any nonequilibrium macroscopic state may be calculated.

Let us consider a system of N identical (noninteracting) particles. For simplicity, the particles are assumed to be spinless. Any eigenvalue of an ideal system is a sum of single particle energies called

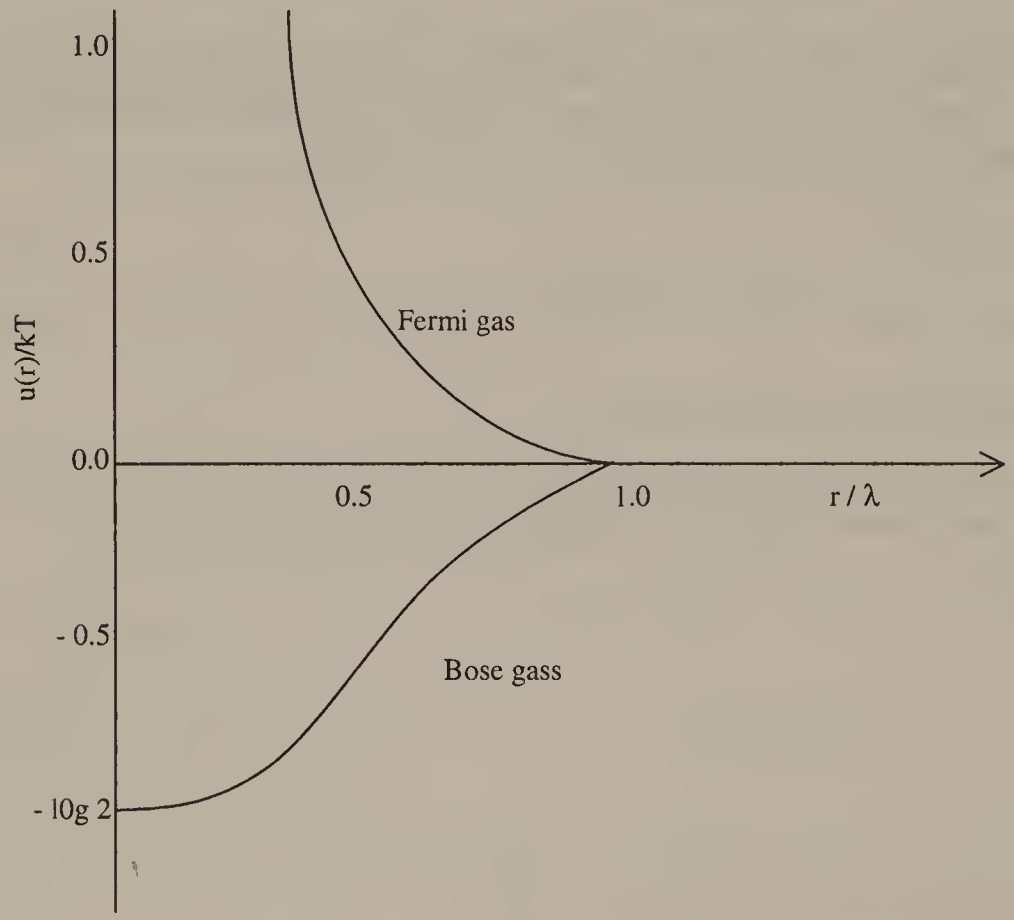


Fig.6.1. The statistical potential $\tilde{u}(r)$ between a pair of particles obeying the Bose-Einsten or Fermi-Dirac statistics as a function of r/λ

levels. These are given by

$$\epsilon_p = p^2/2m \qquad (6.4.1)$$

where m is the mass of a particle and $p = |\mathbf{P}|$, $\mathbf{P}$ being the momentum eigenvalue of the single particles.

Let n_p be the number of particles in a gas, which are in the quantum state with momentum $\mathbf{P}$; the number n_p is sometimes called the occupation number of the various quantum states. A state of an ideal system can be specified by specifying a set of occupation numbers $\{n_p\}$. Hence the total number of particles N and the total energy E of the system are given by

$$N = \sum_P n_p \tag{6.4.2}$$

$$E = \Sigma n_p \in_p \tag{6.4.3}$$

where

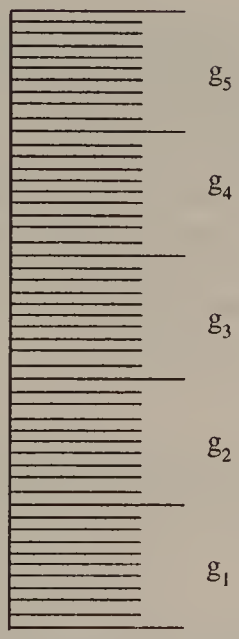


Fig.6.2. Division of the single particle energy level into cell

$n_p = 0, 1, 2, \ldots$ for Boltzmann gas and bosons

$= 0, 1$ for fermions.

In the thermodynamic limit $V \to \infty$, the values of **P** becomes a continuum. Then the energy E forms a continuum spectrum.

Let us divide the energy spectrum of (6.4.3) into groups of states, each group containing respectively g_1, g_2, ... states as shown in Fig.6.2. Each group is called a cell and has an average energy $\in_i$ and number of particles n_i such that

$$N = \sum_P n_i \tag{6.4.4}$$

$$E = \Sigma \in_i n_i \tag{6.4.5}$$

Statistical weight

In order to calculate entropy of the gas, we calculate the statistical weight $\Delta\Gamma$ of a given macroscopic state. Regarding each cell of n_i particles as an independent subsystem, whose statistical weight is $\Delta\Gamma_i$, we can write

$$\Delta\Gamma = \prod_i \Delta\Gamma_i \tag{6.4.6}$$

To calculate the statistical weight $\Delta\Gamma_i$ of the ith cell, it is sufficient to find the number of distinct ways in which n_i particles can occupy the g_i states (levels). Let us calculate the statistical weight for three cases:

Boltzmann gas

In this case the particles are distinguishable. In the ith cell, there are g_i levels. Each of the n_i particles can occupy these levels in g_i ways. Hence n_i particles can occupy the g_i levels in $g_i^{n_i}$ ways. Since the particles are identical, among these distributions, the number of which differ only by permutation of n_i particles is $n_i!$. Hence the statistical weight of the distribution of n_i particles in g_i levels is

$$\Delta\Gamma_i = g_i^{n_i} / n_i! \tag{6.4.7}$$

and the total statistical weight of the system is

$$\Delta\Gamma = \prod_i g_i^{n_i} / n_i! \tag{6.4.8}$$

Bose gas

In this case, the particles are indistinguishable and each level can be occupied by any number of particles. The ith cell has g_i levels with g_i-1 partitions. The statistical weight $\Delta\Gamma_i$ is the number of distinct ways in which n_i particles can be distributed in g_i levels, such that each level may occupy any number of particles; 0, 1, 2, ... In order to calculate this number, we assume the particles as n_i points arranged in a line and separated by (g_i-1) partitions. The total number of positions occupied by particles and partitions is (n_i+g_i-1), out of which n_i positions are selected for the distribution of particles. Since the particles are indistinguishable, the permutations of particles do not change the arrangement. Further, the permutations of partitions among themselves do not alter the levels. Clearly, the statistical weight $\Delta\Gamma_i$ is the number of permutations of n_i particles plus (g_i-1) partitions which give rise to distinct arrangements

$$\Delta\Gamma_i = \{ (n_i + g_i - 1)! / n_i! (g_i - 1)! \} \tag{6.4.9}$$

and

$$\Delta\Gamma = \prod_i \{ (n_i + g_i - 1)! / n_i! (g_i - 1)! \} \tag{6.4.10}$$

Fermi gas

In the Fermi case, no quantum state can accommodate more than one particle. Accordingly, $n_i \leq g_i$. Out of g_i levels, only n_i levels are occupied by one particle each, and the remaining $(g_i - n_i)$ levels are empty. Then $\Delta\Gamma_i$ is the number of ways in which n_i is selected out of the g_i levels. Thus

$$\Delta\Gamma_i = \{ g_i ! / n_i! (g_i - n_i)! \} \tag{6.4.11}$$

and

$$\Delta\Gamma = \prod_i \{ g_i ! / n_i! (g_i - n_i)! \} \tag{6.4.12}$$

Entropy

The entropy S of the system is

$$S = k \ln \Delta\Gamma = k \sum_i \ln \Delta\Gamma_i \tag{6.4.13}$$

Thus, it can be calculated using the values of $\Delta\Gamma_i$ for different systems.

In these calculations we use Stirling's formula when n_i is very large

$$\ln n_i! = n_i \ln n_i - n_i \tag{6.4.14}$$

and neglect unity in comparison to g_i and g_i+n_i in the case of Bose gas. Thus we have the following expressions for the entropy of gases not in equilibrium:

for Boltzmann gas,

$$S/k = \sum_i [n_i \ln g_i - n_i \ln n_i + n_i]$$

$$= \sum_i n_i \ln (eg_i/n_i) \qquad (6.4.15)$$

for Bose gas;

$$S/k = \sum_i [(n_i + g_i) \ln (n_i + g_i) - n_i \ln n_i - g_i \ln g_i]$$

$$= \sum_i [n_i \ln (1 + (g_i/n_i)) + g_i \ln (1 + (n_i/g_i))] \qquad (6.4.16)$$

and for Fermi gas,

$$S/k = \sum_i [g_i \ln g_i - n_i \ln n_i - (g_i - n_i) \ln (g_i - n_i)]$$

$$= \sum_i [n_i \ln ((g_i/n_i) - 1) - g_i \ln (1 - (n_i/g_i))] \qquad (6.4.17)$$

Distribution law

Let us calculate the statistics for the most probable distribution of particles among the energy levels, where the entropy must be maximum. Hence

$$\delta(S/k) = 0 \qquad (6.4.18)$$

We use this condition to obtain the equilibrium distribution for different cases in the following sections.

6.5. Maxwell- Boltzmann Statistics

In this case, we sum over all possible numbers of particles in each state i.e. over all values $n_i = 0, 1, 2,$ ..... for each i. Substituting Eq.(6.4.15) in (6.4.18), we get

$$\sum_i \delta n_i \ln ((g_i/n_i) = 0 \qquad (6.5.1)$$

Since the total number of particles N and the total energy E are constant, we have from (6.4.4) and (6.4.5)

$$\sum_i \delta n_i = 0 \qquad (6.5.2)$$

$$\sum_i \epsilon_i \delta n_i = 0 \qquad (6.5.3)$$

Multiplying (6.5.2) and (6.5.3) by α and β, respectively, and subtracting from (6.5.1), which is the usual method of Lagrange's undermined multipliers, we get

$$\sum_i \delta n_i [\ln (g_i/n_i) - \alpha - \beta \epsilon_i] = 0 \qquad (6.5.4)$$

This is possible only when each term in the sum is separately zero i.e.

$$\ln (g_i / n_i) = \alpha + \beta \epsilon_i$$

$$\text{or} \quad n_i = g_i / \exp(\alpha + \beta \epsilon_i) \tag{6.5.5}$$

where α and β are constants. They are related to temperature T and chemical potential μ as shown in Sec.6.11, by

$$\beta = 1 / kT$$

$$\alpha = \mu / kT \tag{6.5.6}$$

where k is the Boltzmann constant.

Finally (6.5.5) can be expressed as

$$n_i = g_i / \exp [(\epsilon_i - \mu) / kT] \tag{6.5.7}$$

This is known as the Maxwell Boltzmann (MB) statistics or distribution law. Hence the mean occupation number in a state i is written as

$$\langle n_i \rangle = n_i / g_i = \exp [(\mu - \epsilon_i) / kT] \tag{6.5.8}$$

6.6. Bose- Einstein Statistics

In this case it is necessary only to sum over all possible number of particles in each state i.e. $n_i = 0, 1, 2, \ldots$ for each i.

In this case, the substitution of (6.4.16) into (6.4.18) gives

$$\sum_i \delta n_i [\ln (1 + (g_i / n_i))] = 0 \tag{6.6.1}$$

In this case also the total number particles N and the total energy E are constants, we get from (6.4.4) and (6.4.5)

$$\sum_i \delta n_i = 0 \tag{6.6.2}$$

$$\sum_i \epsilon_i \delta n_i = 0 \tag{6.6.3}$$

Multiplying (6.6.2) and (6.6.3) by α and β, respectively, and subtracting from (6.6.1), we get

$$\sum_i \delta n_i [\ln (1 + (g_i / n_i)) - \alpha - \beta \epsilon_i] = 0 \tag{6.6.4}$$

This is possible only when

$$n_i = g_i / (\exp(\alpha + \beta \epsilon_i) - 1) \tag{6.6.5}$$

where α and β are constants. Using the values of $\alpha = \mu/kT$ and $\beta = 1/kT$, (6.6.5) could be expressed as

$$n_i = g_i / (\exp [(\epsilon_i - \mu) / kT] - 1) \tag{6.6.7}$$

This is known as the Bose- Einstein (BE) statistics or distribution law. It is applicable to a system, whose wave function is symmetric and spin of particle is zero or integer multiple of $\hbar$. Then the mean occupation number is given by

$$\langle n_i \rangle = n_i / g_i = 1 / (\exp [(\mu - \epsilon_i) / kT] - 1) \tag{6.6.8}$$

6.7. Photon Statistics

Photons have spin zero and obey the Bose-Einstein statistics. However the total number of particles in this case are not fixed, because the photon can be readily absorbed and emitted by the walls of a container. Hence one obtain 'photon statistics' as the special case of the Bose-Einstein statistics.

In this case from (6.4.4) and (6.4.5), we have

$$\sum_i \delta n_i \neq 0 \tag{6.7.1}$$

$$\sum_i \epsilon_i \delta n_i = 0 \tag{6.7.2}$$

In this case also from (6.4.16) and (6.4.18), we get

$$\sum_i \delta n_i [\ln (1 + (g_i / n_i))] = 0 \tag{6.7.3}$$

Multiplying (6.7.2) by β and substracting form (6.7.3), we get

$$\sum_i \delta n_i [\ln (1 + (g_i / n_i)) - \beta \epsilon_i] = 0 \tag{6.7.4}$$

This is possible only when

$$\ln (1 + (g_i / n_i)) = \beta \epsilon_i$$

or
$$n_i = g_i / (\exp(\beta \epsilon_i) - 1) \tag{6.7.5}$$

This gives an expression for the mean occupation number

$$\langle n_i \rangle = n_i / g_i = 1 / (\exp(\beta \epsilon_i) - 1) \tag{6.7.6}$$

where $\beta = 1/kT$. This is known as the 'Photon Statistics'.

6.8. Fermi- Dirac Statistics

Here one has to sum over the two possible values $n_i = 0, 1$ for each i.
In this case, substituting (6.4.17) into (6.4.18), we get

$$\sum_i \delta n_i \ln ((g_i / n_i) - 1) = 0 \tag{6.8.1}$$

In this case, the total number of particles N and total energy are fixed, so we get from (6.4.4) and (6.4.5)

$$\sum_i \delta n_i = 0 \tag{6.8.2}$$

$$\sum_i \epsilon_i \delta n_i = 0 \tag{6.8.3}$$

Multiplying (6.8.2) and (6.8.3) by α and β, respectively, and subtracting from (6.8.1), we get

$$\sum_i \delta n_i [\ln ((g_i/n_i) - 1) - \alpha - \beta\epsilon_i] = 0 \tag{6.8.4}$$

which gives

$$\ln ((g_i/n_i) - 1) - \alpha - \beta\epsilon_i = 0$$

or $$n_i = g_i / (\exp(\alpha + \beta\epsilon_i) + 1) \tag{6.8.5}$$

Substituting the values of constants α and β, we express (6.8.5) in the form

$$n_i = g_i / \exp [(\epsilon_i - \mu) / kT] + 1 \tag{6.8.6}$$

This is known as the Fermi- Dirac (FD) statistics or distribution law. It is applicable to a system whose wave function is antisymmetric and spin of particle is half odd integer (in the unit of $\hbar$), (6.8.6) gives an expression for the mean occupation number

$$\langle n_i \rangle = n_i / g_i = 1/ (\exp [(\epsilon_i - \mu)/kT] + 1) \tag{6.8.7}$$

6.9. Validity of Maxwell- Boltzmann Statistics

The MB, BE and FD statistics, discussed above, can be expressed in a single form as

$$n_i = g_i / (\exp [(\epsilon_i - \mu) / kT] + J) \tag{6.9.1}$$

where

$$\begin{aligned} J &= 0 && \text{for Boltzmann} \\ &= -1 && \text{for Bose} \\ &= +1 && \text{for Fermi} \end{aligned} \tag{6.9.2}$$

This expression represents the most probable distribution of particles of the various energy levels of the ith cell. If g_i/n_i is very large in comparison to unity, we may write

$$g_i/n_i \approx g_i/n_i \pm 1 \tag{6.9.3}$$

Thus, for large g_i/n_i, both quantum distributions approach to the Boltzmann distribution. This corresponds to the case for $(\epsilon_i - \mu) >> kT$. Hence the Boltzmann statistics is valid if this condition is fulfilled. Thus one arrives at the conclusion that, if the concentration is sufficiently low or if the temperature is sufficiently high, then

$$\exp [(\epsilon_i - \mu) / kT] >> 1$$

and $\langle n_i \rangle \equiv n_i/g_i << 1$ (6.9.4)

In this limits, the quantum statistics reduces to

$$\langle n_i \rangle = \exp [-(\epsilon_i - \mu) / kT] \quad (6.9.5)$$

which is the MB statistics in the classical limit.

A gas in the classical limit is said to be 'non-degenerate'. On the other hand the quantum gas, obeying the BE and FD statistics, is said to be 'degenerate'.

6.10. Thermodynamic Functions

From (6.9.1) all the thermodynamic functions can be derived. Thus the total number of particles is obtained from (6.4.4) as

$$N = z \sum_i g_i \exp(-\beta\epsilon_i) \quad \text{(Boltzmann)}$$

$$= \sum_i g_i / (z^{-1} \exp(\beta\epsilon_i) \mp 1) \quad \text{(Bose, Fermi)} \quad (6.10.1)$$

where

$$z = e^{-\beta\mu} \quad (6.10.2)$$

is known as fugacity. Similarly (6.4.5) gives expressions for the total energy of the system

$$E = z \sum_i g_i \epsilon_i \exp(-\beta\epsilon_i) \quad \text{(Boltzmann)}$$

$$= \sum_i g_i\epsilon_i / (z^{-1} \exp(\beta\epsilon_i) \mp 1) \quad \text{(Bose, Fermi)} \quad (6.10.3)$$

Substituting (6.9.1) in Eq.(6.4.15) – (6.4.17) we have explicit expressions for entropy:

$$S/k = z \sum_i g_i \exp(-\beta\epsilon_i) [\beta\epsilon_i - \ln z + 1] \quad \text{(Boltzmann)}$$

$$= \sum_i g_i[((\beta\epsilon_i - \ln z)/(z^{-1} \exp(\beta\epsilon_i) - 1)) - \ln(1 - z \exp(-\beta\epsilon_i))] \quad \text{(Bose)}$$

$$= \sum_i g_i[((\beta\epsilon_i - \ln z)/(z^{-1} \exp(\beta\epsilon_i) + 1)) - \ln(1 + z \exp(-\beta\epsilon_i))] \quad \text{(Fermi)} \quad (6.10.4)$$

It is easily seen from (6.10.4) that when

$$z \exp(-\beta\epsilon_i) \equiv \exp(\mu - \epsilon_i) / kT << 1$$

the Bose and Fermi expressions reduce to the Boltzmann expression for entropy.

Let us discuss the Boltzmann gas explicity. In the thermodynamic limit, $V \to \infty$, the summation can be changed into integration. Thus from (6.10.1) and (6.10.3), the total number of particles and the total energy of the Boltzmann gas can be written as

$$N = z \int_0^\infty \exp(-\epsilon/kT)\, g(\epsilon)\, d\epsilon \tag{6.10.5}$$

$$E = z \int_0^\infty \exp(-\epsilon/kT)\, \epsilon\, g(\epsilon)\, d\epsilon \tag{6.10.6}$$

The number of quantum states for the entire volume V in the momentum range p and p+dp is

$$g(p)\, dp = (4\pi V/h^3)\, p^2 dp$$

Using (6.4.1) the number of quantum states with the energy range ϵ and $\epsilon + d\epsilon$ is given by

$$g(\epsilon)d\epsilon = (2\pi V/h^3)\,(2m)^{3/2}\,\epsilon^{1/2}\, d\epsilon \tag{6.10.7}$$

Substituting this value in (6.10.5) and integrating over ϵ, we get the total number of particles in tne gas as

$$N = (2\pi Vz/h^3)\,(2m)^{3/2} \int_0^\infty e^{-\epsilon/kT}\, \epsilon^{1/2}\, d\epsilon$$

$$= zV(2\pi mkT/h^2)^{3/2} = zV/\lambda^3 \tag{6.10.8}$$

where

$$\lambda = (2\pi\hbar^2/mkT)^{1/2} \equiv (h^2/2\pi mkT)^{1/2} \tag{6.10.9}$$

is the thermal wavelength. Then the fugacity z is determined as

$$z = (N\lambda^3/V) = \rho\lambda^3 \tag{6.10.10}$$

where $\rho = N/V$

The total energy of the gas is

$$E = (2\pi Vz/h^3)\,(2m)^{3/2} \int_0^\infty \exp(-\epsilon/kT)\, \epsilon^{3/2}\, d\epsilon$$

$$= (3/2)\,(zVkT/\lambda^3) = (3/2)\,NkT \tag{6.10.11}$$

From (6.10.4) the entropy of the Boltzmann gas is

$$S/k = \beta E - N \ln z + N$$

$$= (5/2)N - N \ln [(N/V)\,(h^2/2\pi mkT)^{3/2}] \tag{6.10.12}$$

This is the Sackur- Tetrode equation. Similarly, other thermodynamical properties can also be calculated. Thus, the Helmholtz free energy is

$$A = E - ST = NkT [\ln z - 1] \tag{6.10.13}$$

Substituting (6.10.10) in (6.10.13), we get

$$A = -NkT \ln [(eV/N) (2\pi mkT/h^2)^{3/2}] \tag{6.10.14}$$

and the pressure is

$$P = -(\partial A/\partial V)_N = NkT/V$$

or

$$PV = NkT \tag{6.10.15}$$

Finally the Gibbs free energy is

$$G = A + PV = -NkT \ln [(V/N) (2\pi mkT/h^2)^{3/2}] \tag{6.10.16}$$

and the chemical potential is

$$\mu = -kT \ln [(kT/P) (2\pi mkT/h^2)^{3/2}] \tag{6.10.17}$$

The Boltzmann gas is not a real physical system. It is an approximate model for the Bose and Fermi gases at high temperature.

6.11. Evaluation of Constants α and β

Let us give the physical interpretation of the constants α and β. Substituting Eq.(6.5.5) in (6.4.5) the entropy for the Boltzmann gas is

$$S/k = \sum_i [n_i (\alpha + \beta \epsilon_i) + n_i] = N\alpha + \beta E + N$$

$$= N \ln Q + N \ln N + \beta E + N \tag{6.11.1}$$

where we have used the relation

$$N = \sum_i g_i \exp(-\alpha - \beta \epsilon_i) = \exp(-\alpha) Q \tag{6.11.2}$$

$$Q = \sum_i g_i \exp(-\beta \epsilon_i) \tag{6.11.3}$$

Here Q is the partition function of a particle of energy ϵ_i and degeneracy g_i.
From (6.11.1), we get

$$(\partial S/\partial E)_{N,V} = (\partial S/\partial E)_{N,Q} = \beta k \tag{6.11.4}$$

$$(\partial S/\partial N)_{E,V} = (\partial S/\partial N)_{E,Q} = k \ln (Q/N) = \alpha k \tag{6.11.5}$$

Using the thermodynamic relation

$$dS = (1/T)\, dE + (P/T)\, dV - (\mu/T)\, dN \tag{6.11.6}$$

where μ is the chemical potential, we have

$$(\partial S/\partial E)_{N,V} = 1/T \tag{6.11.7}$$

$$(\partial S/\partial N)_{E,V} = -(\mu/T) \tag{6.11.8}$$

On comparision, finally, we get

$$\beta = (1/kT) \tag{6.11.9}$$

$$\alpha = -(\mu/kT) \tag{6.12.10}$$

6.12. The Ideal Gases in Grand Canonical Ensemble

We may apply the Gibbs distribution for the grand canonical ensemble to derive the distribution laws for an ideal gas. This is obtained from the grand canonical partition function

$$\Xi = \sum_N \sum_n \exp((\mu N - E_{nN})/kT) \tag{6.12.1}$$

where E_{nN} denotes the energy eigenvalue of the system consisting of N particles and μ is the chemical potential per particle. Now, if n_i be the number of particles in the single-particle energy state ϵ_i, then the total number of particles N and total energy values $E(=E_{nN})$ can be expressed as

$$N = \sum_i n_i \tag{6.12.2}$$

$$E = \sum n_i \epsilon_i \tag{6.12.3}$$

Here i denotes a single state, and not the set of degenerate states which may have the same energy. Then the grand canonical partition function may be written as

$$\Xi = \sum_{\{n_i\}} g(n_i) \exp\left[\sum_i n_i(\mu - \epsilon_i) / kT\right] \tag{6.12.4}$$

where $g(n_i)$ is the statistical weight for the distribution of set $\{n_i\}$, and the summation extends over all the sets with the condition (6.12.2). The statistical weight in the various cases is given by

$$g(n_i) = \prod_i G(n_i) \tag{6.12.5}$$

with

$$G(n_i) = (1/n_i!) \quad \text{(Boltzmann)} \tag{6.12.6}$$

$$G(n_i) = 1 \quad \text{(Bose)} \tag{6.12.7}$$

$$G(n_i) = 1 \quad \text{if } n_i = 0 \text{ or } 1 \text{ (Fermi)} \tag{6.12.8}$$

$$= 0 \quad \text{otherwise}$$

Equations (6.12.6) – (6.12.8) can be obtained straight away from Eqs. (6.4.9) - (6.4.13), respectively, by putting $g_i = 1$.

Substituting (6.12.5) in (6.12.4) and reversing the order of Σ and Π, we get

$$\Xi = \prod_i \sum_{n_i} G(n_i) \exp(n_i(\mu - \epsilon_i) / kT \,]) \tag{6.12.9}$$

From the definition of the thermodynamic potential, we have

$$\Omega = -kT \ln \Xi = \sum_i \Omega_i \tag{6.12.10}$$

where

$$\Omega_i = -kT \sum_{\{n_i\}} G(n_i) \exp(n_i(\mu - \epsilon_i) / kT \,) \tag{6.12.11}$$

The mean occupation number of particles in the ith quantum state is

$$\langle n_i \rangle = -(\partial \Omega_i / \partial \mu) \tag{6.12.12}$$

Maxwell-Boltzmann gas

Let us calculate the mean occupation number $\langle n_i \rangle$ for the Maxwell-Boltzmann gas. In this case the statistical weight $G(n_i)$ is given by Eq.(8.12.6). Substituting this value in Eq.(6.12.4)

$$\Xi = \prod_i \sum_{n_i=0}^{\infty} (1/n!) \exp \,[n_i(\mu - \epsilon_i) / kT \,]$$

$$= \prod_i \exp \,(\exp \,[(\mu - \epsilon_i) / kT \,]) \tag{6.12.13}$$

which yields

$$\Omega_i = -kT \exp[(\mu - \epsilon_i) / kT \,] \tag{6.12.14}$$

and

$$\langle n_i \rangle = \exp[\,(\mu - \epsilon_i)/kT \,] \tag{6.12.15}$$

This is the Maxwell-Boltzmann statistics, according to which the mean number of particles occupying a certain quantum state is proportional to the probability that one particle is in that state.

Bose-Einstein gas

In this case, particles are identical and indistinguishable. Hence we obtain

$$\Xi = \prod_i \sum_{n_i=0}^{\infty} \exp \,[n_i(\mu - \epsilon_i) / kT \,]$$

$$= \prod_i 1/\{1 - \exp \,((\mu - \epsilon_i) / kT \,)\} \tag{6.12.16}$$

which yields

$$\Omega_i = kT \ln (1 - \exp [(\mu - \epsilon_i) / kT]) \tag{6.12.17}$$

Thus from (6.12.12), the mean occupation number has the form

$$\langle n_i \rangle = 1/\{\exp ((\epsilon_i - \mu)/ kT) - 1\} \tag{6.12.18}$$

which is the distribution function for an ideal gas, which obeys the Bose-Einstein statistics.

Fermi Dirac gas

In this case, according to Pauli's exclusion principle, occupation number of each state can take only the values 0 and 1. Hence we have

$$\Xi = \prod_i \sum_{n_i=0}^{1} \exp [n_i(\mu - \epsilon_i) / kT]$$

$$= \prod_i [1 + \exp ((\mu - \epsilon_i) / kT)] \tag{6.12.19}$$

and hence

$$\Omega_i = -kT \ln [1 + \exp((\mu - \epsilon_i)/kT)] \tag{6.12.20}$$

Substituting this value in (6.12.12), we obtain an expression for the mean

$$\langle n_i \rangle = 1/\{\exp ((\epsilon_i - \mu)/ kT) + 1\} \tag{6.12.21}$$

This is the distribution function for an ideal gas, which obeys Fermi-Dirac statistics. It is easily seen that when

$$\exp[(\mu - \epsilon_i)/ kT] \ll 1$$

Equations (6.12.18) and (6.12.21) approach the MAxwell-Boltzmann distribution function.

6.13. Ideal Boltzmann Gas

Let us consider an ideal gas which obeys Boltzmann statistics. We have a system of identical particles, each of mass m, confined to a space of volume V and in thermal equilibrium at a temperature T. Since there is no intermolecular interaction to be taken into account, the energy of the system is

$$H(q,p) = \sum_i p_i^2/2m \tag{6.13.1}$$

Then, the partition function is expressed as

$$Q_N = (1/N!) [Q_1]^N \tag{6.13.2}$$

where

$$Q_1 = (1/h^3) \int \exp(-p_i^2/2mkT)\, dp_i dq_i = V [2\pi mkT/h^2]^{3/2} \tag{6.13.3}$$

This gives the free energy as

$$A = -NkT \ln [Q_1] + kT \ln N!$$

Since N is very large, we use Stiring's formula

$$\ln N! = N \ln N - N \qquad N \ln (N/e)$$

which gives

$$A = -NkT \ln [(eV/N) (2\pi mkT/h^2)^{3/2}] \tag{6.13.4}$$

This formula enables us to calculate the free energy of any classical gas of identical particles obeying Boltzmann statistics.

In quantum statistics, we can write (6.13.4) in the form

$$A = -NkT \ln [(e/N) \sum_i \exp (-\epsilon_K/kT)] \tag{6.13.5}$$

where ϵ_K is the energy value of a particle.

Equation (6.13.4) can be rewritten in the

$$A = -NkT \ln (eV/N) - (3/2)NkT \ln(kT) - (3/2)\, NkT \ln (2\pi m/h^2) \tag{6.13.6}$$

Hence the pressure of the gas is

$$P = -(\partial A/\partial V) = NkT/V$$

or

$$PV = NkT \tag{6.13.7}$$

which is the familiar equation of state for an ideal gas.

The entropy of the ideal gas is given by

$$S = -(\partial A/\partial T)$$

$$= (3/2)\, Nk + Nk \ln [(eV/N) (2\pi mkT/h^2)^{3/2}]$$

$$= Nk \ln [(e^{5/2}V/N) (2\pi mkT/h^2)^{3/2}] \tag{6.13.8}$$

or

$$S/k = (5/2)\, N + N \ln [(V/N) (2\pi mkT/h^2)^{3/2}] \tag{6.13.9}$$

which is known as the Sackur-Tetrode equation and is identical to the previous expression (6.10.8). Finally, the energy is

$$U = A + ST = (3/2)\, NkT \tag{6.13.10}$$

Thus we see that the energy of an ideal gas is a function of temperature only. The specific heat per atom at constant volume is

$$c_v = (3/2)\, k \tag{6.13.11}$$

Lastly the Gibbs free energy is given by

$$G = A + PV = -NkT \ln [(V/N) (2\pi mkT/h^2)^{3/2}] \quad (6.13.12)$$

and the chemical potential

$$\mu = -kT \ln [(V/N) (2\pi mkT/h^2)^{3/2}]$$

$$= -kT \ln [(kT/P) (2\pi mkT/h^2)^{3/2}] \quad (6.13.13)$$

which can be conventionally written as

$$\mu = \mu_0 (T) + kT \ln P \quad (6.13.14)$$

6.14. Ideal Gas of Molecules with Internal Motion

In the previous section, we have considered only the translational motion of the molecule. When the internal motion of the molecules is taken into account, the energy of a molecule may be written as

$$\epsilon = (p^2/2m) + \epsilon_K \quad (6.14.1)$$

where the first term is the kinetic energy of the translational motion and ϵ_K is the energy associated with an internal state of motion.

The partition function in this case is given by

$$Q_N = (1/N!) [Q_1 (V,T)]^N \quad (6.14.2)$$

where

$$Q_1(V, T) = Q_{tr} Q_{in} \quad (6.14.3)$$

Q_{tr} is the translational partition function of a molecule, and is given by

$$Q_{tr} = [V (2\pi mkT/h^2)^{3/2}] \quad (6.14.4)$$

while the factor Q_{in} is the partition function corresponding to the internal motion. It may be written as

$$Q_{in}(T) = \sum_k g_K \exp(-\epsilon_K/kT) \quad (6.14.5)$$

where g_K represents the degeneracy of that state.

The free energy in this case is

$$A = -NkT \ln [(eV/N) (2\pi mkT/h^2)^{3/2} Q_{in}]$$

$$= A_{tr} + A_{in} \quad (6.14.6)$$

where

$$A_{tr} = -NkT \ln [(eV/N) (2\pi mkT/h^2)^{3/2}] \quad (6.14.7)$$

is the free energy due to the translational motion and

$$A_{in} = -NkT \ln Q_{in}(T) \tag{6.14.8}$$

is the contribution due to the internal motion of the molecules. Thus the calculation of the free energy of an ideal gas requires an explicit expression for $Q_{in}(T)$ from a knowledge of the internal states of the molecules.

For this purpose, the internal state of a molecule is determined by (i) the electronic state, (ii) the nuclear state, (iii) the vibrational state and (iv) the rotational state. They can be treated independently of one another. Then we write

$$Q_{in}(T) = Q_e Q_n Q_{vib} Q_{rot} \tag{6.14.9}$$

For the free atoms, the only internal states are the electronic states and these for all practical purposes may be replaced by the ground state degeneracy with energy ϵ, then (6.14.5) reduces to

$$Q_{in}(T) = g \exp(-\epsilon/kT) \tag{6.14.10}$$

and hence the free energy becomes

$$A = -NkT \ln [(eV/N) (2\pi mkT/h^2)^{3/2} g \exp(-\epsilon/kT)] \tag{6.14.11}$$

The pressure

$$P = NkT / V$$

is unchanged. The Gibbs free energy is

$$G = A+PV = -NkT \ln[(V/N)(2\pi mkT/h^2)^{3/2} g \exp(-\epsilon/kT)] \tag{6.14.12}$$

and the chemical potential

$$\mu = -kT \ln [(kT/P) (2\pi mkT/h^2)^{3/2} g \exp(-\epsilon/kT)] \tag{6.14.13}$$

6.15. Monatomic Ideal Gases

For a monatonic gas, the contribution of the internal quantum states to the partition function is restricted to the electronic angular momentum and the nuclear spin factor. A single particle has no vibrational or rotational energy, so the internal partition function is given by

$$Q_{in} = Q_e Q_n \tag{6.15.1}$$

where Q_e is the electronic partition function and Q_n the nuclear spin partition function.

The free energy of the monatomic gas is

$$A = -NkT \ln [(eV/N) (2\pi mkT/h^2)^{3/2}] + A_e + A_n \tag{6.15.2}$$

where

$$A_e = -NkT \ln Q_e \tag{6.15.3}$$

$$A_n = -NkT \ln Q_n \tag{6.15.4}$$

A_e and A_n are the conributions to the free energy due to the electronic angular momentum and nuclear spin, respectively.

We now consider monatomic gases, when the temperature is not too high, where the number of ionised atoms in the gas is negligible. This corresponds to the condition $kT \ll E_{ion}$, where E_{ion} is the ionisation energy. At these temperatures the number of atoms in the excited states is also negligible, because the separation between the first excited state and the ground state is generally comparable to the ionisation energy. Thus at temperatures $T \ll E_{ion}/k$, we may regard all the the atoms of the gas to be in the (electronic) ground state.

Let us now consider the simplest case of atoms, namely, the atoms of the inert gases which in their ground state have neither orbital angular momentum nor spin (L=S=0). The ground state is not degenerate and the electronic partition function is

$$Q_e = \exp(-\epsilon_0/kT)$$

For monatomic gas, we put $\epsilon_0 = 0$, so that $Q_e = 1$ and hence $A_e = 0$.

If we ignore the effect of the nuclear spin, the free energy is given by the first term of Eq.(6.15.2) only This gives the specific heat per atom:

$$c_v = (3/2)k \tag{6.15.5}$$

and chemical constant

$$\xi = (3/2) \ln (2\pi m/h^2) \tag{6.15.6}$$

This value of specific heat is due to the translational degrees of freedom of the atom. The electronic degrees of freedom under this condition have no effect on the thermodynamic functions.

If on the other hand, $L = 0$ and $S \neq 0$ in the ground state of the atoms, as for example, in the case of alkali atoms, then in this case also the ground state has no fine structure. The level with spin S has a degeneracy $g_e = 2S + 1$. As a result, the electronic partition function will be given by

$$Q_e = 2S + 1$$

This will increase the chemical constant by a factor

$$\xi_S = (2S + 1) \tag{6.15.7}$$

However, it will not contribute to the specific heat.

In other cases, the ground state of the atom has a fine structure ($L \neq 0$ and $S \neq 0$). Let the total angular momentum of the atom (with given orbital angular momentum L and spin S) be J. Each level with a given J is $(2J + 1)$ – fold degenerate and is denoted by e_J. The electronic partition function may be written as

$$Q_e = \sum_j (2J + 1) \exp(-\epsilon_J/kT) \tag{6.15.8}$$

The summation is taken over all possible values of J for the given L and S.

From this, we can obtain expressions in the following limiting cases:

(i) when temperature is high, so that $kT \gg \epsilon_J$, then we can put

$$\exp(-\epsilon_J/kT) \quad 1$$

and

$$Q_e = (2L + 1)(2S + 1)$$

The electronic motion in this case also makes no contribution to the specific heat but add a quantity

$$\xi_{LS} = \ln[(2L + 1)(2S + 1)]$$

to the chemical constant.

(ii) When the temperature is small, so that $kT \ll \epsilon_J$. In this case all the terms may be neglected in the sum (6.15.8) except $\epsilon_J = 0$ (the lowest state of the atom), then

$$Q_e = (2J_0 + 1)$$

where J_0 is the total angular momentum of the atom in the ground state. As a consequence, the quantity

$$\xi_J = \ln[2J_0 + 1]$$

is added to the chemical constant, but the specific heat remains constant.

Thus when the ground state of the atom has fine structure, the specific heat of the gas has the constant value (3/2)Nk at very low and very high temperatures. However, at immediate temperatures it depends on the temperature and passes through a maximum.

Let us now consider the effect of nuclear spin i, which causes the hyperfine splitting of atomic levels. The corresponding degeneracy is (2i + 1). The energy differences between the hyper fine components are so small as to be neglected in calculating the partition function. Accordingly, the nuclear partition function becomes

$$Q_n = 2i + 1$$

This term changes the chemical constant by

$$\xi_n = \ln(2i + 1)$$

but does not affect the specific heat.

6.16. Diatomic Ideal Gases

In the previous section, we have considered monatomic gases at temperatures for which kT is small compared to the ionisation energy and all the atoms are in the ground state. In this section we consider diatomic gases at temperatures for which kT is small compared to the energy of dissociation. At these temperatures, the number of dissociated molecules in the gas is negligible. Thus, we may regard all the molecules of the gas to be in the lowest electronic state.

In the case of diatomic molecules, the internal partition function includes the contribution from the vibrational and rotational degrees of freedom in addition to the factors due to the electronic angular momentum and nuclear spin. The effect of the nuclear spin is appreciable only for the diatomic

molecules composed of like atoms, such as isotope of hydrogen (H_2 and D_2). This effect is negligible for the diatomic molecules composed of unlike atoms such as HCl.

Let us consider the simple case, where the gas molecule in the lowest electronic state has neither orbital angular momentum nor spin ($\Lambda = 0$, $S = 0$); such an electronic state has no fine structure.

The energy level of diatomic molecule is the sum of three independent parts – the electronic energy, vibrational energy, and rotational energy. For a singlet electronic state, it can be written as

$$\epsilon = \epsilon_0 + \epsilon_{vib} + \epsilon_{rot} \tag{6.16.1}$$

where ϵ_0 is the electronic energy, ϵ_{vib} the vibrational energy, and ϵ_{rot} the rotational energy.

The internal partition function is given by

$$Q_{in} = \exp(-\epsilon_0/kT)\, Q_{vib}\, Q_{rot} \tag{6.16.2}$$

where the vibrational and rotational partition functions are defined as

$$Q_{vib} = \sum_j g_v \exp(-\epsilon_{vib}/kT) \tag{6.16.3}$$

$$Q_{rot} = \sum_k g_K \exp(-\epsilon_{rot}/kT) \tag{6.16.4}$$

Accordingly the free energy of the diatomic gas is

$$A = A_{tr} + A_{vib} + A_{rot} \tag{6.16.5}$$

where A_{tr}, A_{vib} and A_{rot} are respectively the translational, vibrational, and rotational parts.

$$A_{tr} = -NkT \ln[(eV/N)(2\pi mkT/h^2)^{3/2}] + N\epsilon_0 \tag{6.16.6}$$

$$A_{vib} = -NkT \ln Q_{vib} \tag{6.16.7}$$

$$A_{rot} = -NkT \ln Q_{rot} \tag{6.16.7'}$$

The total specific heat of the molecule is

$$C_V = C_{tr} + C_{vib} + C_{rot}$$

$$C_P = C_{tr} + C_{vib} + C_{rot} + 1$$

which arise, respectively, due to the translational, vibrational, and rotational motions of atoms within the molecule.

Let us discuss each part separately.

1. The Translational part

The translational part of the free energy is given by Eq.(6.16.6) from which the translational energy is

$$U_{tr} = N\epsilon_0 + (3/2)NkT \tag{6.16.8}$$

This is a linear function of temperature. The specific heat per molecule is

$$C_{tr} = (3/2)\,k \tag{6.16.9}$$

which is constant.

2. The vibrational part

When the temperature is not very high, the oscillations of atoms are small in amplitude and hence harmonic. The vibrational enegy is then given by

$$\epsilon_{vib} = \hbar\omega(v + (1/2)) \tag{6.16.10}$$

where $\hbar\omega$ is the vibrational quantum, and $v \equiv 0,1,2, \ldots$, the vibrational quantm number. Since the degeneracy of each vibrational energy level of different frequencies is unity, $g_v = 1$, and the vibrational partition function is given by

$$Q_{vib} = \sum_v \exp(-\hbar\omega\,(v + (1/2))/kT)$$

$$= \exp(-\sigma_v/2)/(1 - \exp(-\sigma_v)) \tag{6.16.11}$$

where

$$\sigma_v = \theta_v/T \quad \text{and} \quad \theta_v = \hbar\omega/k$$

is called the characteristic vibrational temperature of the molecule (see Table 6.1)

Table 6.1. Vibrational and Rotational Temperature (in K)

	H_2	HD	D_2	HCl	N_2	O_2	Cl_2	Br_2	I_2
θ_v	6100	5226	4307	4140	3340	2230	798	462	307
θ_r	85.4	64.3	43.0	15.2	2.9	2.1	0.36	0.12	0.05

Substituting this value in Eq.(6.16.7) the free energy is

$$A_{vib} = (1/2)\,N\hbar\omega + NkT\ln(1 - \exp(-\sigma_v)) \tag{6.16.12}$$

the entropy is

$$S_{vib} = -Nk\ln(1 - \exp(\sigma_v)) + Nk\sigma_v\,(1/(\exp(\sigma_v) - 1)) \tag{6.16.13}$$

the energy is

$$U_{vib} = (1/2)\,N\hbar\omega + N\hbar\omega\,(1/(\exp(\sigma_v) - 1)) \tag{6.16.14}$$

and the specific heat per molecule is

$$C_{vib} = k(\hbar\omega/kT)^2\,(e^{\hbar\omega/kT}/(e^{\hbar\omega/kT} - 1)^2) \tag{6.16.15}$$

From this we can calculate the values for the two limiting cases.

(i) At low temperatures ($kT << \hbar\omega$) Eq.(6.16.15) reduces to

$$C_{vib} = k(\hbar\omega/kT)^2 e^{-\hbar\omega/kT}$$

giving

$$C_{vib} \to 0, \quad \text{as } T \to 0$$

The vibrational degrees of freedom are then said to be frozen.

(ii) At high temperatures ($kT \gg \hbar\omega$), we can write (6.16.15) as

$$C_{vib} = k\,(\hbar\omega/kT)^2 \{(1 + (\hbar\omega/kT) + (1/2)(\hbar\omega/kT)^2 + ...) / [(\hbar\omega/kT) + (1/2)(\hbar\omega/kT)^2 + ...]^2 \}$$

$$= k\,\{(1+(\hbar\omega/kT) + (1/2)(\hbar\omega/kT)^2+...) / (1+ (1/2)(\hbar\omega/kT)+ ...)^2\}$$

which gives

$$C_{vib} \to k, \quad \text{as } T \to \infty.$$

Thus the contribution due to the vibrational degree of freedom to the specific heat of a diatomic gas is zero at low temperatures, and k at high temperatures. In the intermediate range of temperature, it varies between 0 and k as shown in Fig.6.3.

3. The Rotational part

The rotational energy of a diatomic molecule is given by

$$\epsilon_{rot} = \hbar^2 K(K + 1) / 2I \qquad (6.16.16)$$

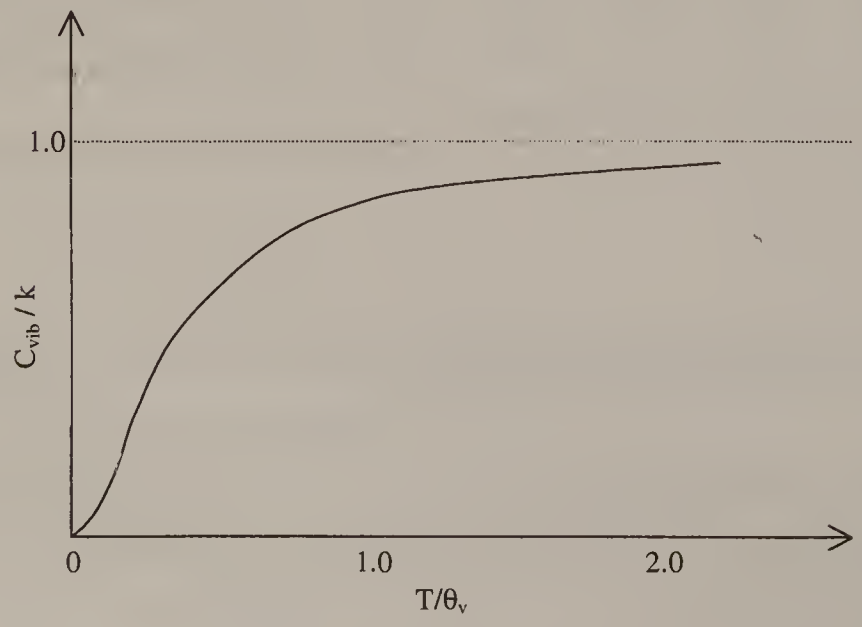


Fig.6.3. The vibrational specific heat C_{vib} of a diatomic gas as a function of T/θ_v

where K is the rotational quantum number and $I = mr_0^2$ is the moment of inertia of the molecule. Here $m = m_1m_2/(m_1 + m_2)$ is the reduced mass of the two atoms and r_0 the equilibrium distance between them. The degeneracy of each rotational level is $g_k = (2K + 1)$. Hence the rotational partition is given by

$$Q_{rot} = \sum_{K=0}^{\infty} (2K + 1) \exp(-\hbar^2K(K+1)/2IkT)$$

$$= \sum_{K=0}^{\infty} (2K + 1) \exp(-K(K+1)\, \sigma_r) \qquad (6.16.17)$$

where

$$\sigma_r = \theta_r/T$$

and

$$\theta_r = \hbar^2/2Ik$$

is called the characteristic rotational temperature (see Table 6.1)

One can use (6.16.17) to calculate the rotational free energy. Let us calculate it for two limiting cases:

(i) At low temperatures ($T \ll \hbar/2Ik$), we keep the first two terms of the sum only. Thus

$$Q_{rot} = 1 + 3 \exp(-2\sigma_r) \qquad (6.18.18)$$

The free energy in this case is approximated as

$$A_{rot} = -NkT \ln [1 + 3\exp(-2\sigma_r)]$$

$$-3NkT \exp(-2\sigma_r) \qquad (6.18.19)$$

Hence the entropy

$$S_{rot} = 3Nk [1 + 2\sigma_r] \exp (-2\sigma_r) \qquad (6.16.20)$$

the energy is

$$U_{rot} = A_{rot} + S_{rot}\, T$$

$$= 6Nk\, \theta_r \exp (-2\theta_r/T) \qquad (6.16.21)$$

and the specific heat per mol is

$$C_{rot} = 12\, k\, (\theta_r/T)^2 \exp (-2\theta_r/T) \qquad (6.16.22)$$

Thus $C_{rot} \to 0$ as $T \to 0$. Hence at low temperature, a diatomic gas behaves like a monatomic gas. Thus at low temperatures, the rotational degrees of freedom are also frozen.

(ii) At high temperatures ($T \gg \hbar^2/2Ik$), the rotational energy may be approximated by a continuum and the summation in (6.16.17) is replaced by an integration

$$Q_{rot} = \int_0^\infty (2K + 1) \exp(-K(K+1)\sigma_r)\, dK = T/\theta_r \qquad (6.16.23)$$

The free energy then becomes

$$A_{rot} = -NkT \ln T + NkT \ln \theta_r \qquad (6.16.24)$$

the entropy becomes

$$S_{rot} = Nk + Nk \ln (T/\theta_r) \qquad (6.16.25)$$

the energy becomes

$$U_{rot} = NkT \qquad (6.16.26)$$

and the specific heat per mol becomes

$$C_{rot} = k \qquad (6.16.27)$$

In general, the rotational specific heat C_{rot} is calculated using Eq.(6.16.17). The variation of C_{rot} with T is shown in the Fig.6.4. The rotational specific heat has a maximum value of 1.1 k at $T = 0.81\theta_r$, and then tends asymptotically to the classical value k.

The disagreement with experimental results (not shown in the Fig.6.4) is observed at the intermediate temperatures; in particular it never rises above k as predicted by the theory. This discrepancy can be explained by taking the nuclear spin into consideration.

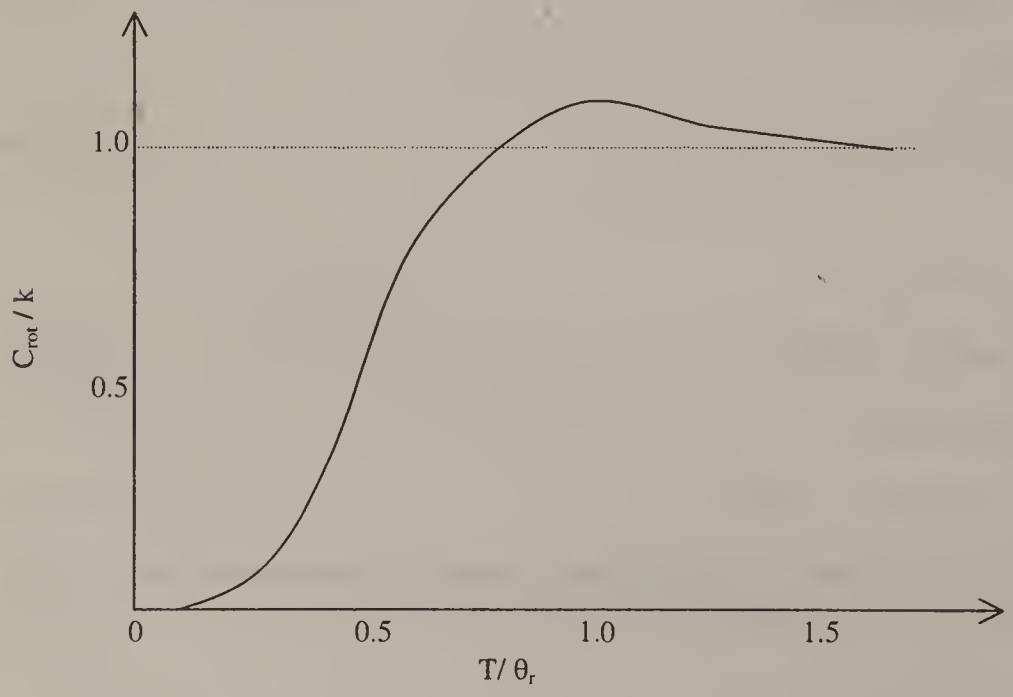


Fig.6.4. The rotational specific heat C_{rot} of a diatomic gas as a function of T/θ_r

At this stage it is relevant to mention that for a diatomic gas the vibrational part of the thermodynamic properties becomes important at considerably higher temperatures than the rotational part. At very low temperatures (when rotational as well as vibrational degrees of freedom of the the molecules are frozen), we have

$$C_V = (3/2)\,k \qquad C_P = (5/2)\,k$$

As the temperature increases, the rotational degrees of freedom begin to loosen and the specific heat increases to (5/2)k at $T \gg \theta_r$. This value will prevail right up to $T = \theta_v$. Accordingly, for $\theta_r \ll T \ll \theta_v$

$$C_V = (5/2)\,k \qquad C_P = (7/2)\,k$$

At $T = \theta_v$, the specific heat will again increase because the vibrational degree of freedom will start loosening. At $T \gg \theta_v$, the vibrational degrees of freedom are also fully excited, and we have

$$C_V = (7/2)\,k \qquad C_P = (9/2)\,k$$

The specific heat of a diatomic ideal gas as a function of temperature is shown in Fig.6.5. Such a dependence of specific heat on temperature is in fact observed experimentally.

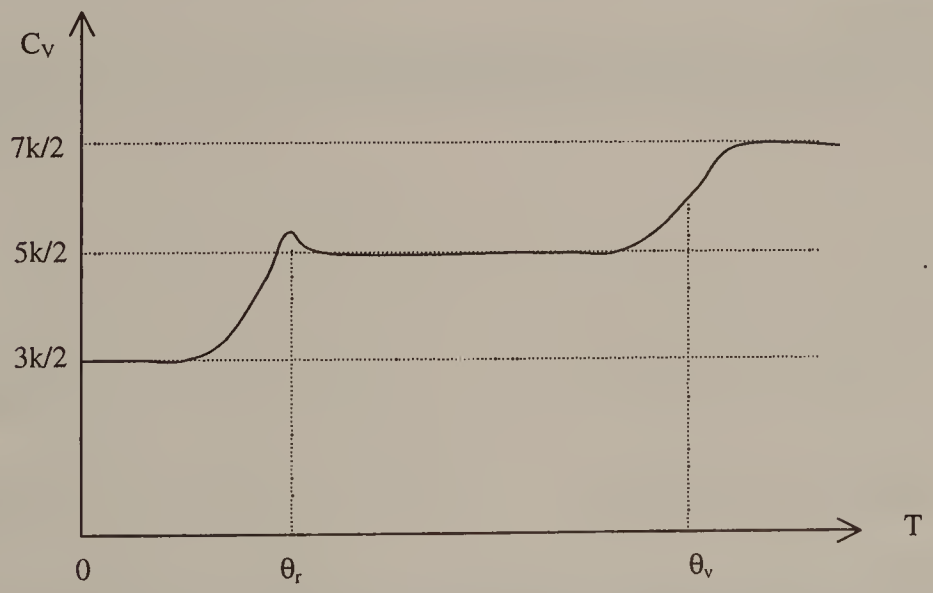


Fig.6.5. The specific heat of a diatomic gas

4. Effect of nuclear spin

The effect of nuclear spin is important for diatomic molecules of like atoms, such as two isotopes of hydrogen (H_2 and D_2). On the other hand, it is unimportant in the case of diatomic molecules of unlike atoms.

Let us consider a diatomic molecules of like atoms with nuclear spin i, which causes the hyperfine splitting of atomic levels. The resultant spin I of the diatomic molecule can then be 2i, 2i-1, ..., 1, 0. Out of this, the even and odd total nuclear spins I are associated with even and odd value of K, respectively (K being the rotational quantum number).

The number partition function for the parallel nuclear spin is

$$Q_n = (i + 1)(2i + 1)$$

and for the antiparallel spin

$$Q_n^{\#} = i(2i + 1)$$

So the relative nuclear partition function for even and odd total nuclear spins are

$$Z_{even} = i/(2i + 1)$$

$$Z_{odd} = (i + 1)/(2i + 1)$$

for a half-integral spin i and

$$Z_{even} = (i + 1) / (2i + 1)$$

$$Z_{odd} = i / (2i + 1)$$

for integral spin i. Accordingly, the rotational partition function for such a molecule can be modified as

$$Q_{rot} = Z_{even}\, Q_{even} + Z_{odd}\, Q_{odd} \qquad (6.16.28)$$

where

$$Q_{even} = \sum_{k=0,2,...} (2K + 1) \exp(-K(K + 1)\, \sigma_r)$$

$$Q_{odd} = \sum_{k=1,3,...} (2K + 1) \exp(-K(K + 1)\, \sigma_r) \qquad (6.16.29)$$

$$A_{rot} = -NkT \ln [Z_{even}\, Q_{even} + Z_{odd}\, Q_{odd}] \qquad (6.16.30)$$

At high temperatures,

$$Q_{even} \quad Q_{odd} \quad (1/2)Q_{rot} = T/2\, \theta_r \qquad (6.16.31)$$

which leads to the classical approximation for the free energy. Hence at high temperature, the specific heat of a diatomic molecule is k and does not depend on the nature of atoms associated with a molecule.

At lower temperatures the situation is different. The gas may be regarded as a mixture of two components with even and odd total nuclear spins.

For hydrogen isotopes, molecules with greater nuclear statistical weight are known as orthohydrogen molecules, and those with lower nuclear statistical weight are known as parahydrogen molecules. Thus for H_2 and D_2, the nuclear partition functions are

$$\begin{aligned} H_2\,(i = 1/2) &\begin{cases} \text{ortho} & Z_{odd} = 3/4 \\ \text{para} & Z_{even} = 1/4 \end{cases} \\ D_2\,(i = 1) &\begin{cases} \text{ortho} & Z_{odd} = 2/3 \\ \text{para} & Z_{even} = 1/3 \end{cases} \end{aligned} \tag{6.16.32}$$

The relative concentrations of the ortho and para in equilibrium are determined by the relative magnitude of the two parts of the partition function (6.16.28). Thus, the ortho to para ratio is given by

$$n_{H_2} = (N_{ortho}\text{–}H_2)/(N_{para}\text{–}H_2) = Z_{odd}Q_{odd}/Z_{even}Q_{even} = 3Q_{odd}/Q_{even} \tag{6.16.33a}$$

$$n_{D_2} = (N_{ortho}\text{–}D_2)/(N_{para}\text{–}D_2) = Z_{even}Q_{even}/Z_{odd}Q_{odd} = 2Q_{even}/Q_{odd} \tag{6.16.33b}$$

As $T \to 0$, all the molecules tend to be in the lowest rotational state with $K = 0$, and the H_2 gas is wholly para while D_2-gas is wholly ortho. At high temperatures where Q_{even} Q_{odd}, this value is three for H_2 and two for D_2. At intermediate temperatures, one has to use (6.16.33) to calculate the thermodynamic properties of a gas.

As the temperature varies from 0 to ∞, the ratios vary from 0 to 3 and 0 to 2 for H_2 and D_2, respectively. However for all practical purposes we take these ratios to be equal to three for H_2 and two for D_2. Hence the hydrogen and deutorim gases are taken as a mixture of the ortho and para in the ratio of 3:1 and 2:1, respectively i.e,

$$N_{H_2} = (3/4)\,N_{ortho} + (1/4)\,N_{para} \tag{6.16.34a}$$

$$N_{D_2} = (2/3)\,N_{ortho} + (1/3)\,N_{para} \tag{6.16.34b}$$

Accordingly the specific heat is given as

$$(C_{rot})_{H_2} = (3/4)\,C_{ortho} + (1/4)\,C_{para} \tag{6.16.35a}$$

$$(C_{rot})_{D_2} = (2/3)\,C_{ortho} + (1/3)\,C_{para} \tag{6.16.35b}$$

The calculated values of C_{para}, C_{ortho} and C_{rot} for H_2 and D_2 are shown in Fig.6(a,b). Curves 1 and 2 represent C_{para} and C_{ortho} respectively while curve 3 corresponds to C_{rot} calculated from (6.16.35). The experimental results are also shown in the figure. The agreement between theory and experiment is fairly good.

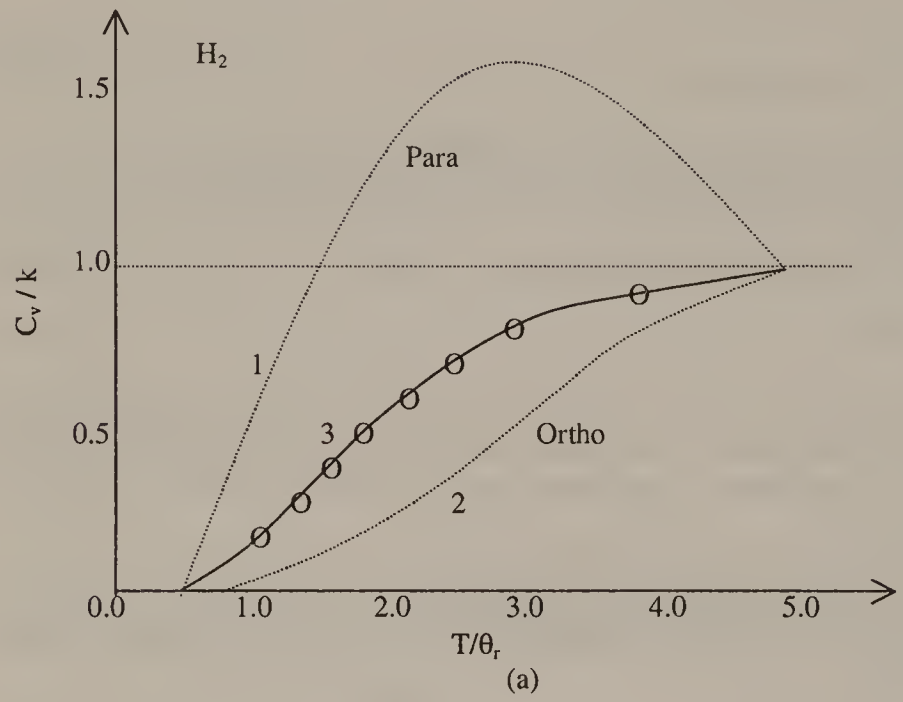
5. Effect of electronic angular momentum

So far we have considered the diatomic molecules in the lowest electronic state ($\Lambda = 0$, $S = 0$) where $g_e = 1$. However, certain molecules have, in their lowest electronic state, either (i) non-zero orbital angular momentum ($\Lambda \neq 0$), (ii) non-zero spin ($S \neq 0$) or (iii) both non-zero ($\Lambda \neq 0$, $S \neq 0$).

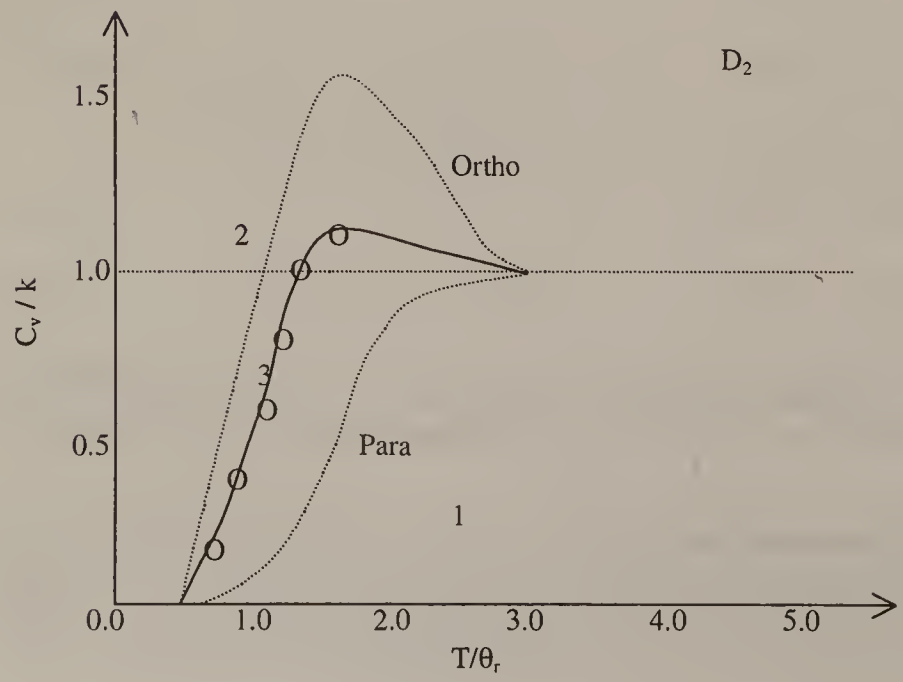
When $\Lambda \neq 0$ and $S = 0$, there is two-fold degeneracy corresponding to the two possible directions of the orbital angular momentum relative to the molecular axis, then as a result $g_e=2$. This adds a quantity

$$\xi_\Lambda = \ln 2$$

to the chemical constant.



(a)



(b)

Fig.6.6. The theoretical values of the specific heat of mixtures of (a) para and ortho H_2 and (b)para and ortho D_2.The experimental values are represented by points (not in scale)

For $\Lambda = 0$ and $S \neq 0$, the degeneracy is $(2S+1)$ and the chemical constant is increased by

$$\xi_S = \ln (2S + 1)$$

In both these cases, the energy and hence the specific heat remain unchanged. When $\Lambda \neq 0$, $S \neq 0$, the fine structure occurs. The interval of the fine structure is generally of the order of kT, which should be taken into account in calculating the thermodynamic functions. In case of a doublet fine structure, the electronic partition function is given by

$$Q_e = g_0 + g_1 e^{-\Delta/kT} \tag{6.16.36}$$

where g_0 and g_1 are the degeneracy factors of the doublet and Δ is their separation energy. Then, the free energy for an electronic part is

$$A_e = -NkT \ln [g_0 + g_1 e^{-\Delta/kT}] \tag{6.16.37}$$

From this, we obtain an expression for the electronic specific heat as

$$C_e = k(\Delta/kT)^2 / ([1 + (g_0/g_1)e^{\Delta/kT}] [1 + (g_1/g_0)e^{-\Delta/kT}] \tag{6.16.38}$$

which must be added to other parts of the specific heat. From (6.16.38) it is clear that $C_e \to 0$ when $T \to 0$ and $T \to \infty$, and has a maximum value k for T Δ/k.

6.17. Ideal Paramagnetism

We consider a system of particles, such as electrons, which have a resultant magnetic dipole moment. When a magnetic field is applied, the magnetic dipoles tend to orient themselves in the direction of the applied magnetic field, giving rise to paramagnetism. For convenience, the system may be treated as an ideal gas obeying the Maxwell-Boltzmann statistics.

We consider a system of N identical (noninteracting) particles, each of mass m, placed in a magnetic field **B**, and at a temperature T. Since there is no interparticle interaction to be taken into account, the Hamiltonian of the system is given by

$$H = H_0(p_i,q_i) + \sum_{i=1}^{N} \epsilon_i \tag{6.17.1}$$

where $H_0(p_i,q_i)$ is the Hamiltonian of the system in the absence of an external magnetic field and ϵ_i is the energy of the ith particle, which arises due to the presence of a magnetic field **B** and is given by

$$\epsilon_i = -\mu_i .\mathbf{B} \tag{6.17.2}$$

μ is an intrinsic moment of a particle.

The partition function of the system is given by

$$Q_n = Q_n^0 \{\Sigma \exp [\Sigma_i \mu_i.\mathbf{B}/kT] \} \tag{6.17.3}$$

where the summation goes over all sets of orientations of the system, and Q_n^0 is the partition function of the system in the absence of an external field. Equation (6.17.3) can be rearranged to give

$$Q_n = Q_n^0 \left[\prod_{i=1}^{N} \Sigma \exp(\mu_i.\mathbf{B}/kT) \right] = Q_n^0 [Q_1^B]^N \tag{6.17.4}$$

where

$$Q_1^B = \Sigma \exp(\mu_i.\mathbf{B}/kT) \tag{6.17.5}$$

is the single-dipole partition function. Here the summation is extended over the orientation of a particle with respect to the magnetic field **B**.

The mean magnetic moment per unit volume along the direction of the external magnetic field is

$$\langle M \rangle = (1/V) \langle -\partial H/\partial B \rangle = kT (\partial/\partial B) [\ln Q_N/V] \tag{6.17.6}$$

In the grand canonical ensembles, $\langle M \rangle$ is expressed as

$$\langle M \rangle = kT (\partial/\partial B) [\ln \Xi / V] \tag{6.17.7}$$

The magnetic susceptibility per unit volume of a system is defined as

$$\chi_T = \partial \langle M \rangle / \partial B \tag{6.17.8}$$

For a diatomic substance $\chi < 0$ while for a paramagnetic substance $\chi > 0$.

First, we calculate the partition function classically. If the orientation of the particle be denoted by (θ,φ), then

$$\mu.\mathbf{B} = \mu B \cos\theta$$

and the single-dipole partition function can be written as

$$Q_1^B = \int_0^{2\pi} \int_0^{\pi} e^{\beta \mu B \cos\theta} \sin\theta \, d\theta \, d\varphi$$

$$= 2\pi \int_{-1}^{1} e^{\beta \mu B x} \, dx$$

$$= 2\pi [(e^{\beta \mu B} - e^{-\beta \mu B})/\beta \mu B]$$

$$= 4\pi (\sinh(\beta \mu B)/\beta \mu B) \tag{6.17.9}$$

Substituting (6.17.4) and (6.17.9) in (6.17.6)

$$\langle M \rangle = (NkT/V) (\partial/\partial B) [\ln Q_1^B]$$

$$= (N\mu/V)\,[\coth(\beta\mu B) - (1/\beta\mu B)]$$

$$= \rho\mu\, L(a) \qquad (6.17.10)$$

where $\rho = N/V$ is the number density and L(a) is the Langevin function.

$$L(a) = \coth(a) - (1/a) \qquad (6.17.11)$$

with

$$a = \beta\mu B$$

Then, the mean magnetic moment per particle is

$$\langle\mu\rangle = (\langle M\rangle/\rho) = \mu L(a) \qquad (6.17.12)$$

For small magnetic field **B** and at high temperature T, a is very small and (6.17.12) reduces to

$$\langle\mu\rangle/\mu = L(a) \quad a/3$$

On the other hand, for large **B** and at low temperature, a is large, thus

$$\langle\mu\rangle/\mu = L(a) \quad 1$$

If we plot L(a) against a, we get a curve shown in Fig.6.7, whose gradient at the origin is 1/3, and it reaches the maximum value of L(a) = 1 asymptotically.

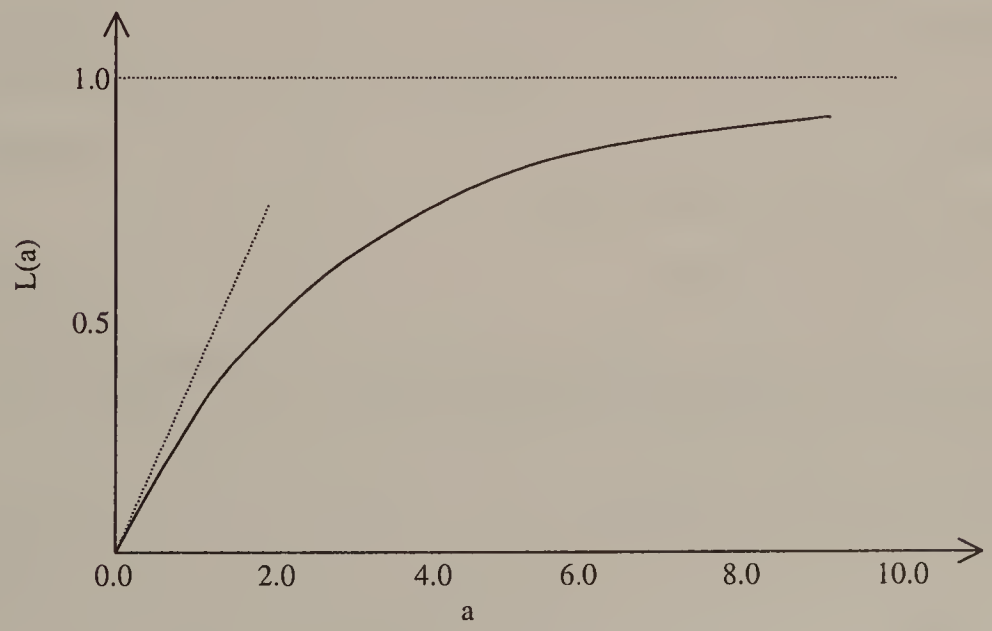


Fig.6.7. The Langevin function L(a) as a function of a.

Substituting Eq.(6.17.10) in Eq.(6.17.8) we obtain an expression for the magnetic susceptibility per unit volume of the system:

$$\chi_T = (\rho\mu^2/kT) [(1/a^2) - \text{cosech}^2(a)] \quad (6.17.13)$$

Expanding in terms of a, we obtain a high temperature expansion for χ_T as

$$\chi_T = (\rho\mu^2/3kT) [1 - (1/12) (\mu B/kT)^2 + ...] \quad (6.17.14)$$

when $B \to 0$ and/or $T \to \infty$, Eq. (6.17.14) reduces to

$$\chi_T = \rho\mu^2/3kT = C/T \quad (6.17.15)$$

where

$$C = \rho\mu^2/3k$$

Thus the susceptibility χ_T varies as 1/T, which is the Curie law of paramagnetism. The parameter C is the Curie constant of the system. Curie first of all obtained it from the experimental facts; Langevin, later on, derived it classically.

Brillouin in 1928, treated the problem of paramagnetism quantum mechanically. According to quantum theory, the magnetic moment μ of a particle cannot have an arbitrary value, rather it should be quantised.

It is well known that the ratio of the magnetic moment of a particle to its total angular momentum is g(e/2 mc), i.e. the magnetic moment μ of a particle is

$$\mu = g(e/2mc)J\hbar = g\mu_B J \quad (6.17.16)$$

where

$$\mu_B = e\hbar/2mc \quad (6.17.17)$$

is the Bohr magneton and g is known as Lande's g-factor

$$g = (3/2) + (S(S+1) - L(L+1))/2J(J+1) \quad (6.17.18)$$

Here S, L and J are respectively the spin, orbital and resultant quantum numbers of the particle. If the total angular momentum is due only to the spin of the particle, then g = 2; on the other hand, if it is due only to the orbital motion, then g = 1. In presence of a magnetic field **B**, the energy levels are

$$\epsilon_m = -\boldsymbol{\mu}.\mathbf{B} = -g\mu_B(\mathbf{J}.\mathbf{B}) = -mg\mu_B B \quad (6.17.19)$$

where

$$m = J \cos(\mathbf{J},\mathbf{B})$$

is the magnetic quantum number which has 2J + 1 values: -J, -J+1, ..., J – 1, J in accordance with the rule of space quantization. Then the single-dipole partition function is given by

$$Q_1^B = \sum_{m=-J}^{J} \exp(-\beta \in_m) = \sum_{m=-J}^{J} \exp(\beta m g \mu_B B) \qquad (6.17.20)$$

Introducing a quantity $\gamma = \beta g \mu_B B$, (6.17.20) can be written as

$$Q_1^B = \sum_{m=-J}^{J} e^{my}$$

$$= e^{-J\gamma}[1 + e^{\gamma} + e^{2\gamma} + \ldots + e^{2J\gamma}]$$

$$= e^{-J\gamma}((e^{(2J+1)\gamma} - 1)/(e^{\gamma} - 1))$$

$$= ((e^{(2J+1)\gamma/2} - e^{-(2J+1)\gamma/2})/(e^{\gamma/2} - e^{-\gamma/2}))$$

$$= \sinh[(2J + 1)\,\gamma/2] / \sinh(\gamma/2) \qquad (6.17.21)$$

Then, the mean magnetic moment per particle is

$$\langle \mu \rangle = kT(\partial/\partial B)\,(\ln\{\sinh[(2J + 1)\,\gamma/2]\} - \ln\{\sinh(\gamma/2)\})$$

$$= (g\mu_B J)\,\{((2J+1)/2J)\coth[(2J+1)\,\gamma/2] - (1/2J)\coth(\gamma/2)\}$$

$$= \mu B_J(a) \qquad (6.17.22)$$

where $a = \gamma J = \beta \mu B$ and $B_J(a)$ is the Brillouin function of order J.

$$B_J(a) = ((2J+1)/2J)\coth[(2J+1)\,a/2J] - (1/2J)\coth(a/2J) \qquad (6.17.23)$$

and the mean magnetic moment per unit volume is

$$\langle M \rangle = \rho \langle \mu \rangle = \rho \mu B_J(a)$$

$$= \rho g \mu_B J B_J(g\mu_B JB/kT) \qquad (6.17.24)$$

This is the quantum result for <M>.

With the help of (6.17.8) and (6.17.24), we obtain an expression for χ_T as

$$\chi_T = (\rho(g\mu_B J)^2/kT)\,[(1/2J)^2\,\mathrm{cosech}^2(a/2J) - ((2J+1)/2J)^2\,\mathrm{cosech}^2((2J+1)\,(a/2J))] \qquad (6.17.25)$$

Let us discuss the results for different value of J. We first consider the case of the smallest value, J = ½, which arises from the single-electron spins, and which allows only two orientations. In this case, we have

$$B_{1/2}(a) = 2\coth(2a) - \coth(a) = \tanh(a) \qquad (6.17.26)$$

where $a = \beta \mu_B B$, since for the electron spin, g = 2. Then, the mean magnetic moment per unit volume is

$$\langle M \rangle = \rho\mu_B B_{1/2} (\mu_B B/kT) = \rho\mu_B \tanh (\mu_B B/kT) \quad (6.17.27)$$

and the magnetic susceptibility is

$$\chi_T = (\rho\mu_B^2/kT) \operatorname{sech}^2 (\mu_B B/kT) \quad (6.17.28)$$

Another interesting case is that when J is very large. In this case, Eq.(6.17.23) reduces to

$$\lim_{J\to\infty} B_J(a) = \coth(a) - (1/a) \equiv L(a) \quad (6.17.29)$$

which is the Langevin function defined earlier in Eq.(6.17.11). This function is obtained if dipoles may be in any arbitrary direction. In this case the problem essentially reduce to its classical part.

Let us now consider the magnetic susceptibility for some special cases:

(i) When the magnetic field **B** is small and temperature T is high ($\beta g\mu_B JB \ll 1$), the function B_J can be expressed as

$$\langle \mu \rangle/\mu = B_J(a) \quad (J+1)a/3J \quad (6.17.30)$$

Then,

$$\langle M \rangle = \rho\langle \mu \rangle = \rho(g\mu_B)^2 BJ(J+1)/3kT \quad (6.17.31)$$

and

$$\chi_T = \partial\langle M \rangle/\partial B = \rho(g\mu_B)^2 J(J+1)/3kT = C_J/T \quad (6.17.32)$$

which is Curie law, where the Curie constant C_J is given by

$$C_J = \rho(g\mu_B)^2 J(J+1)/3k = \rho\mu_{eff}^2/3k \quad (6.17.33)$$

where the effective magnetic moment is

$$\mu_{eff} = g\mu_B [J(J+1)]^{1/2} \quad (6.17.34)$$

when $J = \infty$, we get from (6.17.33)

$$C_\infty = \rho\mu^2/3k$$

which is the classical value of the Curie constant.
On the other hand, when J = 1/2, we get

$$C_{1/2} = \rho\mu^2/k = 3\,C_\infty \quad (6.17.35)$$

Thus $C_{1/2}$ is exactly three times the classical value. The variation of C_J with 1/J is shown in Fig.6.8.

(ii) When the magnetic field **B** is large and temperature is low ($g\mu_B JB/kT \gg 1$), we get

$$\langle \mu \rangle/\mu = B_J(a) \quad 1$$

for all J. This means that the magnetisation gets saturated at very high magnetic fields and low temperatures.

The Curie law is generally valid experimentally for paramagnetic salts, such as chromium-potassium alum (J = 3/2, g = 2) and iron-ammonia alum (J = 5/2, g = 2), in weak magnetic fields at high temperatures. The Curie law is violated for the electron gas in metals at ordinary temperatures. This discrepancy was explained by Pauli (1927), who considered the free electrons in metal as a fermion gas obeying Fermi-Dirac statistics, which will be discussed in Sec.8.12 of chapter 8.

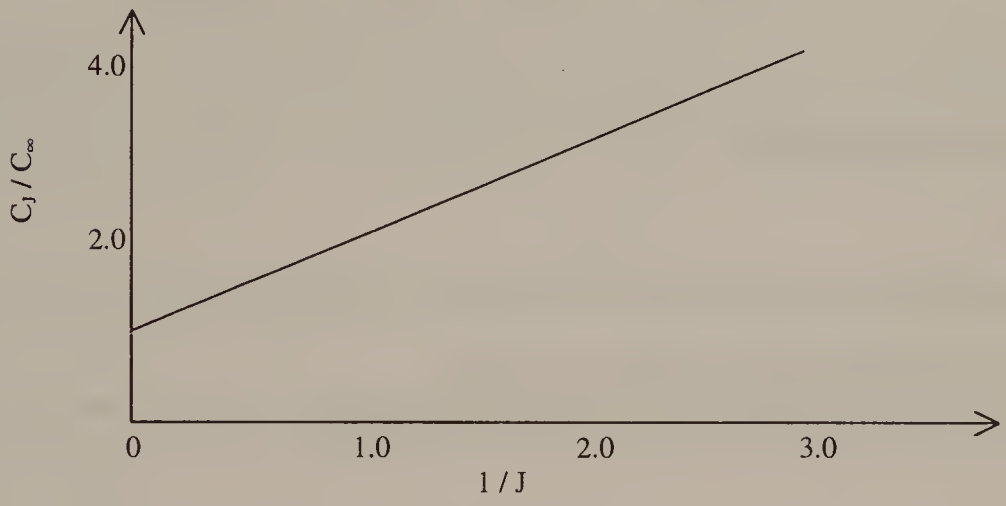


Fig.6.8. The variation of the Curie constant C_J, with J where J is the total quantum number

6.18. Thermodynamic Functions of Magnetic Systems

In this section, we consider the thermodynamic properties of the 'paramagnetic material in the presence of a magnetic field **B**. Treating the problem quantum mechanically, the partition function (6.17.4) for such a system can be written as

$$Q_N = Q_N^0 [\sinh\{(2J+1)a/2J\} / \sinh(a/2J)]^N \qquad (6.18.1)$$

where

$$a = \beta g \mu_B J B = \beta \mu B$$

Once the partition function is known, all the thermodynamic properties of the system in the presence of a magnetic field can be calculated. Thus the free energy of the system is

$$A = A_0 - NkT\,[\ln(\sin\{(2J + 1)\, a/2J\}) - \ln(\sinh\{a/2J\})] \qquad (6.18.2)$$

where A_0 is the free energy due to the Hamiltonian H_0 [see Eq.(6.16.6)]. By differentiation, the entropy is

$$S = -(\partial A/\partial T)_B$$

$$= S_0 + Nk[\ln(\sinh\{(2J + 1)\, a/2J\}) - \ln(\sinh\{a/2J\})]$$

$$- Nk(g\mu_B JB/kT)\,[((2J + 1)/2J)\coth\{(2J + 1)\,a/2J\} - (1/2J)\coth\{a/2J\}] \qquad (6.18.3)$$

and the magnetic moment of the system is

$$M = -(\partial A/\partial B)_T = Ng\mu_B J\,[((2J + 1)/2J)\coth\{(2J + 1)\,a/2J\} - (1/2J)\coth(a/2J)] \qquad (6.18.4)$$

which can also be obtained from Eq.(6.17.24) by the relation M = V<M>, where <M> is the mean magnetic moment per unit volume. The energy is

$$U = A + ST = U_0 - Ng\mu_B JB[((2J + 1)/2J)\coth\{(2J+1)\,a/2J\} - (1/2J)\coth\{a/2J\}]$$

$$= U_0 - MB \qquad (6.18.5)$$

and the specific heat at constant field is

$$C_B = -(\partial U/\partial T)_B$$

$$= C_0 - Nk(g\mu_B JB/kT)^2\,[((2J + 1)/2J)^2\,\mathrm{cosech}^2\{(2J + 1)\,a/2J\} - (1/2J)^2\,\mathrm{cosech}^2\{a/2J\}] \qquad (6.18.6)$$

where C_0 is the specific heat in the absence of the magnetic field.

Equations from (6.18.2) to (6.18.6) provide the results for any value of J. We now consider the important case when J = ½, which arises from the single electron spin. Thus

$$g = 2$$

$$\mu_B = e/2mc = 9.27 \times 10^{-18}\ \mathrm{erg/kG}$$

where m is the mass of electron and kG = 10^3 Gauss. The magnetic moment per particle in this case is $\mu = \mu_B$.

We obtain the results for J = (1/2) from Eqs. (6.18.2) – (6.18.6). Thus,

$$A = A_0 - NkT \ln[2\cosh(\mu B/kT)] \qquad (6.18.7)$$

$$S = S_0 + Nk\,[\ln(2\cosh(\mu B/kT)) - (\mu B/kT)\tanh(\mu B/kT)] \qquad (6.18.8)$$

$$M = N\mu\tanh(\mu B/kT) \qquad (6.18.9)$$

$$U = U_0 + N\mu B\tanh(\mu B/kT) = U_0 - MB \qquad (6.18.10)$$

$$C_B = C_0 + Nk\,(\mu B/kT)^2\,\mathrm{sech}^2(\mu B/kT) \qquad (6.18.11)$$

Let us now consider the magnetic contribution to the thermodynamic properties of the paramagnetic system. In this case

$$A = -NkT\,[\ln(2\cosh(\mu B/kT)\,] \qquad (6.18.12)$$

$$S = Nk\,[\ln(2\cosh(\mu B/kT)) - (\mu B/kT)\tanh(\mu B/kT)] \qquad (6.18.13)$$

$$U = -N\mu B \tanh(\mu B/kT) \qquad (6.18.14)$$

$$C_B = Nk\,(\mu B/kT)^2\,\mathrm{sech}^2(\mu B/kT) \qquad (6.18.15)$$

When the magnetic field B tends to infinity and/or temperature T tends to zero, $\mu B/kT \gg 1$ and $\tanh(\mu B/kT) \to 1$, then we have from (6.18.14)

$$U \to -N\mu B$$

This is expected as in this limit all the magnetic moments tend to be in the state of lower energy ($-\mu B$), leading to $U = -N\mu B$. On the other hand, when the magnetic field B tends to zero and/or temperature tends to infinity, $\mu B/kT \ll 1$ and $\tanh(\mu B/kT) \to 0$, then $U \to 0$. The variation of $U/N\mu B$ with $kT/\mu B$ is shown in the Fig.6.9.

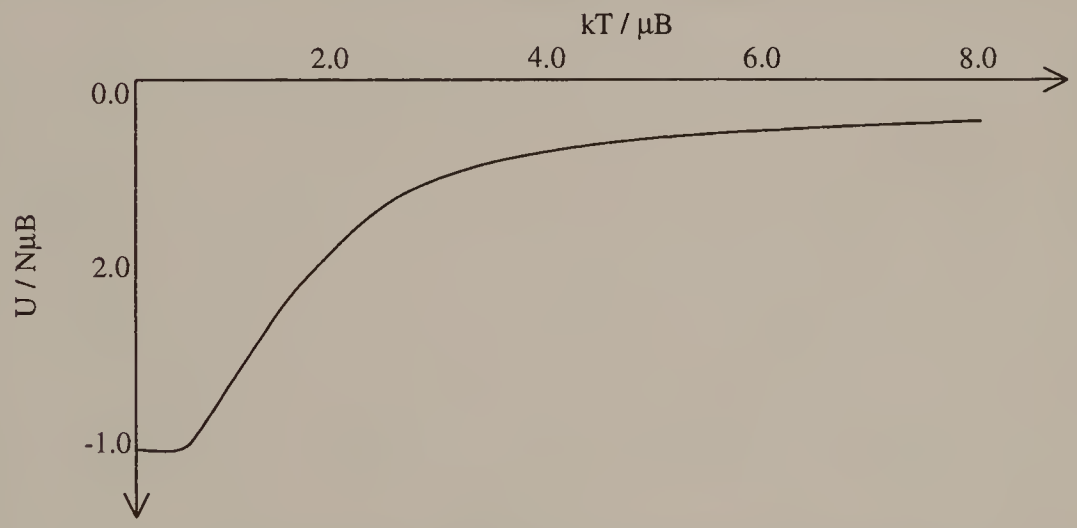


Fig.6.9. The variation of the energy U of a paramagnetic system (with J = ½ with $kT/\mu B$)

The specific heat, given by Eq.(6.18.15), can be written as

$$C_B = NK\,(2\mu B/kT)^2\, e^{2\mu B/kT}\,(1 + e^{2\mu B/kT})^{-2} \qquad (6.18.16)$$

This form of the specific heat is identical to the Schottky specific heat of a two-level system with an energy difference

$$\Delta = 2\mu B$$

At low temperature ($kT \ll \mu B$), Eq.(6.18.16) reduces to

$$C_B = NK\,(2\mu B/kT)^2\, e^{-2\mu B/kT}$$

which gives

$$C_B \to 0, \qquad \text{when} \qquad kT/\mu B \to 0$$

At high temperature ($kT \gg \mu B$), we can write (6.18.16) as

$$C_B = Nk(2\mu B/kT)^2 \left([1 + (2\mu B/kT) + \tfrac{1}{2}(2\mu B/kT)^2 + ...] / [2 + (2\mu B/kT) + \tfrac{1}{2}(2\mu B/kT)^2 + ...]^2\right)$$

which, for large value of $(kT/\mu B)$, gives

$$C_B \quad Nk(\mu B/kT)^2$$

or

$$C_B \propto T^{-2}$$

The variation of C_B/Nk with $(kT/\mu B)$ is shown in Fig.6.10. The specific heat C_B first increases to a maximum value of 0.44 Nk at kT 0.84μB and then begins to decrease.

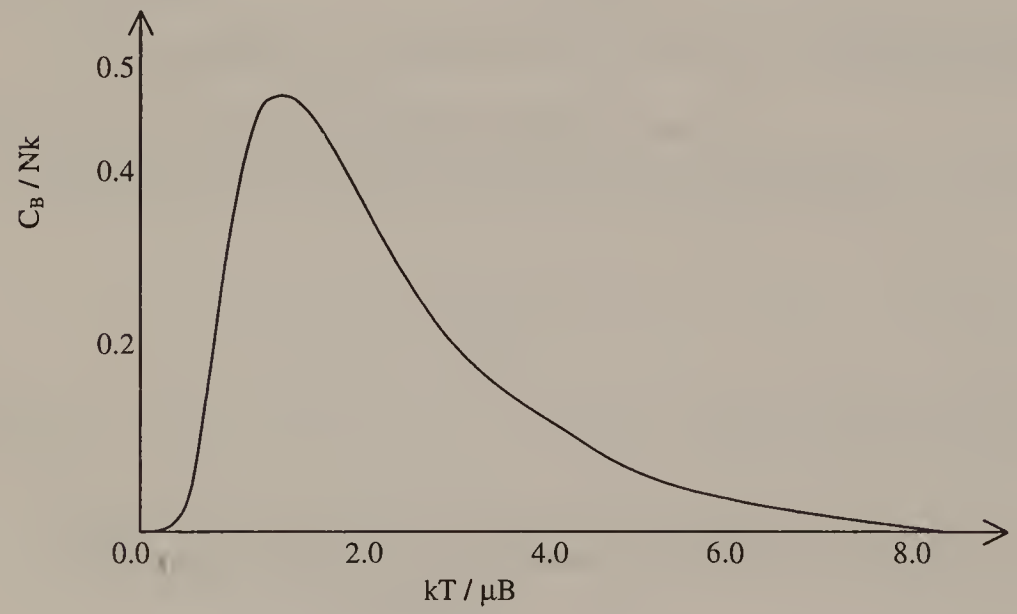


Fig.6.10. The variation of the specific heat C_B of a paramagnetic system (with J = ½) with $kT/\mu B$

Equation (6.18.13) can be rearranged as

$$S/Nk = \ln(1 + e^{-2a}) + 2a / (e^{2a} + 1) \qquad (6.18.17)$$

where $a = \mu B/kT$

At low temperatures ($kT << \mu B$), Eq.(6.18.17) reduces to

$$S/Nk = 2(\mu B/kT)\, e^{-2\mu B/kT}$$

which shows that

$$S \to 0 \qquad \text{when} \quad kT/\mu B \to 0$$

in accordance with the third law of thermodynamics.

At high temperatures ($kT \gg \mu B$), $a \ll 1$, and we can write (6.18.17)

$$S/Nk = \ln [2 - 2a + (1/2)(2a)^2 + ...] + 2a\,[2 + 2a + (1/2)(2a)^2 + ...]^{-1}$$

which gives

$$S/Nk = \ln 2 \quad \text{when } kT/\mu B \to \infty$$

Figure 6.11 demonstrate the variation of S/Nk with $kT/\mu B$.

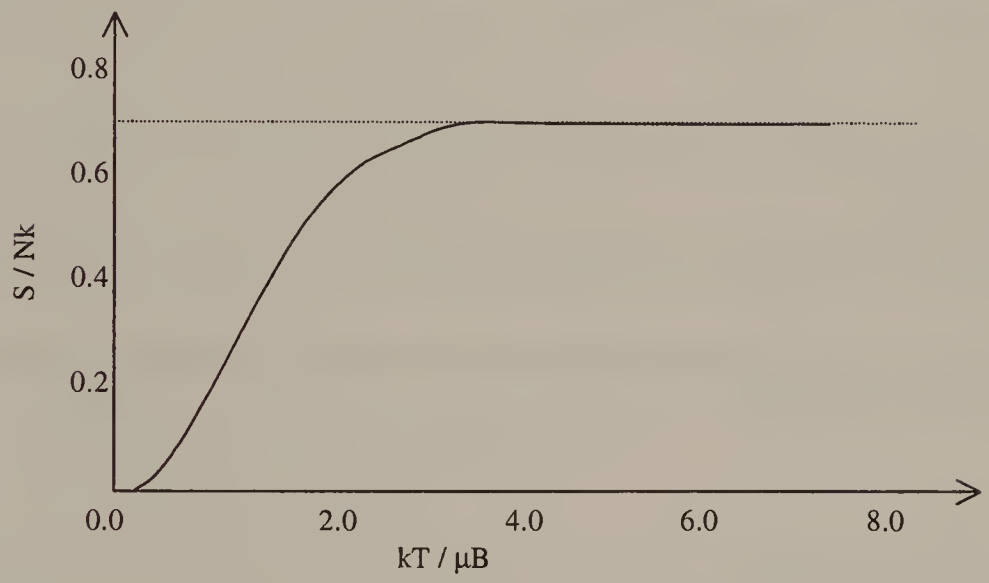


Fig.6.11. The variation of the entropy S of a paramagnetic system (with J = ½) with $kT/\mu B$

Let us now discuss cooling by adiabatic demagnetisation. The entropy S of the paramagnetic system is a function of (B/T). Differentiating (6.18.13) with respect to B at a given T, we get

$$dS/dB = -Nk(\mu/kT)^2\, B\, \text{sech}^2(\mu B/kT)$$

Since $\text{sech}^2(\mu B/kT)$ is always positive, the entropy S decreases with increasing B for a given value of T. This principle is used in the method of adiabatic demagnetisation to produce temperatures below 1 K.

We consider two magnetic fields B_1 and B_2 ($B_2 > B_1$). The entropy S is plotted as a function of T in Fig.6.12 for both the magnetic field B_1 and B_2.

We first increases the magnetic field from B_1 to B_2 under isothermal consideration, at a initial temperature T_i (from state a to state b in Fig.6.12). During this process there is a heat transfer from the paramagnetic specimen to heat bath. The specimen is then thermally isolated and the magnetic field is

reduced very slowly under adiabatic conditions from B_2 to B_1. In this process, the entropy S of the specimen remains constant. This is illustrated in the change from state b to state c in Fig.6.12, leading to the lower temperature T_f. This is cooling by adiabatic demagnetisation.

Since the entropy S is a function of B/T only, this ratio remains constant during adiabatic demagnetisation, i.e. we have

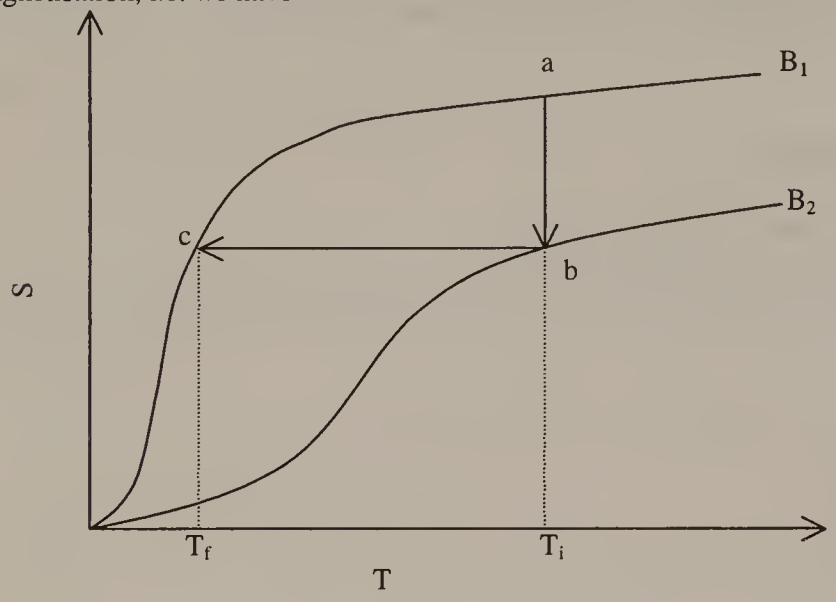


Fig.6.12. The entropy S of a paramagnetic system (with J = ½) as a function of temperature T for the magnetic fields B_1 and B_2 (with $B_2 > B_1$)

$$B_1/T_f = B_2/T_i$$

where T_f is the final temperature. Thus

$$T_f = T_i\,(B_1/B_2)$$

For example, with T_i 1 K and $B_1/B_2 \approx 1/100$, we get the final temperature $T_f \approx 10^{-2}$ K.

So far we have considered only the magnetic aspect of this problem. In addition, the entropy also arises due to the lattice vibrations of the paramagnetic crystal. So the total entropy is the sum of the magnetic entropy and the vibrational entropy. It is the total entropy which is constant during adiabatic demagnetisation. However, the vibrational entropy is negligible at low temperatures. Hence the final temperature of the paramagnetic crystal will be only just above T_f.

Problems

6.1 Distinguish among the postulates of Maxwell-Boltzmann, Bose-Einstein, and Fermi-Dirac statistics.

6.2 Show that in the first approximation the partition function of a system of N non-interacting, indistinguishable particles is given by

$$Q_N = (1/N!\lambda^{3N}) \int\int \exp\left[-\beta \sum_{i<j} \tilde{u}_{ij}\right] \prod_{i=1}^{N} d\mathbf{r}_i$$

where $\tilde{u}_{ij}$ is the statistical potential. Hence calculate the first order correction to the equation of state.

6.3 Prove that the quantum mechanical partition function for a system of N non-interacting, indistinguishable particles approaches the classical form
$Q_N = V^N/N!\lambda^{3N}$
at high temperature

6.4 Derive expression for the distribution functions corresponding to the three statistics. Discuss the conditions for the validity of the respective distribution functions.

6.5 Derive distribution laws for ideal quantum gases, using the grand canonical partition function.

6.6 Show that the entropy of an ideal quantum gas in thermal equilibrium is given by
$S = k\sum_i [-\langle n_i\rangle \ln\langle n_i\rangle \pm \langle 1 \pm n_i\rangle \ln \langle 1 \pm n_i\rangle]$

6.7 Discuss an ideal Boltzmann gas. Show that the entropy for such a gas is given by
$S = Nk [(5/2) - \ln\{(N/V)(h^2/2mkT)^{3/2}\}]$

6.8 Derive an expression for the partition function for an ideal classical gas containing molecules of different components and hence deduce the thermodynamic properties for such a system.

6.9 A gas consists of N_1 molecules of one component and N_2 molecules of another component, such that, $N=N_1+N_2$. Show that the Helmholtz free energy of the system is
$A = NkT [\ln \rho - 1 + x_1 \ln x_1 + x_2 \ln x_2]$
where ρ is the number density and
$x_1 = N_1/N$ and $x_2 = N_2/N$

6.10 Derive the partition function for an ideal extreme relativistic Boltzmann gas and also deduce the equation of state for it.

6.11 An ideal Boltzmann gas is enclosed in a box of volume V. The energy of a single particle of momentum P is
$e_p = (p^2/2m) + mc^2$
calculate the partition function of the gas at temperature T. Also deduce the equation of state for such a gas.

6.12 Derive the partition function for a Boltzmann gas in the n-dimensional space and using it, deduce the equation of state and specific heat of the gas.

6.13 Derive the partition function for hydrogen with nuclear spin ½. Obtain an expression for the equilibrium ratio of ortho and para hydrogen at any temperature.

6.14 Derive the rotational partition function of deuterium with nuclear spin 1. Also deduce rotational specific heat for it.

6.15 Derive an expression for the entropy of a perfect monatomic gas. How is this expression modified in the case of a diatomic gas.

6.16 Discuss the theory of the specific heat of a diatomic gas with special reference to hydrogen. Indicate the nature of agreement of the theory with experiment.

6.17 Derive an expression for the specific heat of diatomic gases. Discuss how the results compare with experiments. How do you account for the discrepancy in the case of hydrogen.

6.18 Discuss the specific heat of a diatomic gas. Explain how the molecules consisting of identical atoms differ from those consisting of nonidentical atoms.

6.19 Discuss Langevin theory of paramagnetism. Show that the high temperature magnetic susceptibility is
$\chi_T = (\rho\mu^2/3kT)\,[\,1 - (1/12)\,(\mu\beta/kT)^2 + \ldots\,]$

6.20 Show that the magnetic moment of a paramagnetic substance is
$\mu = gJ\mu_B B_J(gJ\mu_B B/kT)$
where $B_J(a)$ is the Brillouin function.

6.21 Show that the specific heat of the spin paramagnetism is given by
$C_B = Nk\,(\mu B/kT)^2\,\mathrm{sech}^2\,(\mu B/kT)$

6.22 The Hamiltonian of a paramagnetic substance is
$$H = -\sum_{i=1}^{N} \mu_i.\mathbf{B}$$
Calculate the energy U and entropy S of the system. Find the relation between U and T.

6.23 Consider a paramagnetic substance which obeys the Curie law
$\chi_T = C/T$
and has a specific heat $C_0 = a/T$ at zero magnetisation. Derive the specific at constant magnetic field, C_B, the specific heat at constant magnetisation C_M, and the adiabatic magnetic susceptibility χ_S.

CHAPTER 7

IDEAL BOSE SYSTEMS

Particles having a zero or integral spin (in units of $\hbar$) are called 'bosons'. They include
(i) photon (spin is 1)
(ii) phonons (spin is 1)
(iii) He^4 (spin is zero), and
(iv) mesons (K and π), whose spin is zero.

Bosons are indistinguishable and obey the Bose-Einsten (BE) statistics. We are interested chiefly in photons and He^4 in this chapter and phonons-sound wave quanta in chapter 12.

7.1. Ideal Bose Gas

Let us consider an ideal gas obeying Bose-Einstein statistics. For such a gas the number of molecules in the energy range ϵ and $\epsilon+d\epsilon$ is given by

$$n(\epsilon)d\epsilon = g(\epsilon)d\epsilon / (z^{-1}e^{\beta\epsilon} - 1) \tag{7.1.1}$$

where $\beta = 1/kT$ and z is the fugacity of the gas, related to the chemical potential μ through the formula

$$z = e^{\beta\epsilon} \tag{7.1.2}$$

The energy of a particle is just the kinetic energy of its translational motion, which is given by

$$\epsilon = p^2/2m \tag{7.1.3}$$

The number of quantum states for the entire volume V in the momentum range p and p+dp is

$$g(p)dp = (4\pi V/h^3)p^2dp \tag{7.1.4}$$

where the orientation of the particle due to its spin is not taken into consideration. The spin S of the particle causes $g \equiv (2S+1)$ – fold degeneracy. Taking into account, the number of quantum state is

$$g(p)dp = (4\pi gV/h^3)p^2dp \tag{7.1.5}$$

Using (7.1.3) and (7.1.4), the number of quantum states with the energy range ϵ and $\epsilon+d\epsilon$ is given by

$$g(\epsilon)d\epsilon = (2\pi gV/h^3)\,(2m)^{3/2}\,\epsilon^{1/2}\,d\epsilon \tag{7.1.6}$$

Substituting in (7.1.1) and integrating over ϵ, we get the total number of particles in the gas:

$$N = (2\pi gV/h^3)(2m)^{3/2}\int_0^\infty (\epsilon^{1/2}\, d\epsilon/(z^{-1}e^{\beta\epsilon}-1)) \tag{7.1.7}$$

and the total energy of the gas is

$$U = \int_0^\infty \epsilon\, n(\epsilon)\, d\epsilon$$

$$= (2\pi gV/h^3)(2m)^{3/2}\int_0^\infty (\epsilon^{3/2}\, d\epsilon/(z^{-1}e^{\beta\epsilon}-1)) \tag{7.1.8}$$

From (7.1.7), one can determine the chemical potential μ of the gas as a function of T and N/V. The thermodynamic potential Ω of the system is

$$\Omega = \sum_i \Omega_i = kT \sum_i \ln(1 - e^{\beta(\mu-\epsilon_i)})$$

Changing from summation to integration, we obtain an expression for the thermodynamic potential :

$$\Omega = (2\pi gV/h^3)(2m)^{3/2}(kT)\int_0^\infty d\epsilon\, \epsilon^{1/2} \ln(1 - e^{\beta(\mu-\epsilon)})$$

Integrating by parts, we get

$$\Omega = -(2/3)(2\pi gV/h^3)(2m)^{3/2}\int_0^\infty (\epsilon^{3/2}\, d\epsilon/(z^{-1}e^{\beta\epsilon}-1)) = -(2/3)\, U \tag{7.1.9}$$

Since, $\Omega = -PV$, we have

$$PV = (2/3)\, U \tag{7.1.10}$$

which is exact and valid even in the case of Boltzmann gas.

Putting $\epsilon/kT = x$ in (7.1.7) and (7.1.8), we obtain

$$N = 2\pi gV\,(2mkT/h^2)^{3/2}\int_0^\infty x^{1/2}\, dx/(z^{-1}e^{x}-1) \tag{7.1.11}$$

$$U = 2\pi gVkT\,(2mkT/h^2)^{3/2}\int_0^\infty x^{3/2}\, dx/(z^{-1}e^{x}-1) \tag{7.1.12}$$

One can obtain the equation of state of the gas using Eqs. (7.1.10) – (7.1.12). Let us consider the limiting case of the Boltzmann gas, (where $z \equiv \exp(\mu/kT) \ll 1$). We can expand $(z^{-1}e^{x}-1)^{-1}$ as a series in powers of z, and truncating after the first two terms, evaluate Eqs.(7.1.11) and (7.1.12) as

$$N = 2\pi gV (2mkT/h^2)^{3/2} \int_0^\infty dx\, x^{1/2} ze^{-x} (1 + ze^{-x})$$

$$= gV (2mkT/h^2)^{3/2} [z(1 + (1/2\sqrt{2})z)] \quad (7.1.13)$$

$$U = 2\pi gVkT (2mkT/h^2)^{3/2} \int_0^\infty dx\, x^{3/2} ze^{-x} (1 + ze^{-x})$$

$$= (3/2)\, kTgV (2mkT/h^2)^{3/2} [z(1 + (1/4\sqrt{2})z)] \quad (7.1.14)$$

Using (7.1.13), it can be shown that

$$z = (N/gV) (h^2/2\pi mkT)^{3/2} [1 + (1/2\sqrt{2})z]^{-1}$$

$$(N/gV) (h^2/2\pi mkT)^{3/2} [1 - (1/2\sqrt{2}) (N/gV) (h^2/2\pi mkT)^{3/2}] \quad (7.1.15)$$

We substitute this value in (7.1.14) to obtain an expression for energy:

$$U = (3/2)\, NkT [1 - (1/4\sqrt{2}) (N/gV) (h^2/2\pi mkT)^{3/2}] \quad (7.1.16)$$

where the first term gives the enrgy in the Boltzmann limit and the second term gives the required correction due to the deviation from the classical behaviour.

Substituting (7.1.16) in (7.1.10) we obtain the equation of state

$$PV = NkT [1 - (1/4\sqrt{2}) (N/gV) (h^2/2\pi mkT)^{3/2}] \quad (7.1.17)$$

The correction term depends on the value of the quantity $(N/gV) (h^2/2\pi mkT)^{3/2}$. For spinless particle, g = 1, and the correction term will be small when

$$(N/V) (h^2/2\pi mkT)^{3/2} \ll 1$$

For this N/V should be small, i.e. the gas should be sufficiently rarefied, or the temperature T should be high. At very high temperatures, the correction term will be very small and may be neglected, leading to the classical properties. Thus, we see that the deviations from the classical behaviour occur when the temperature is lowered at constant density. The deviations in this case cause the decrease in the thermodynamic properties, such as pressure and energy, and we may say that there is an 'effective attraction' between the particles.

7.2. Ideal Bose Gas : A Bose-Einstein Condensation

Let us investigate in detail the physical behaviour of an ideal Bose gas. When $\epsilon^{\mu/kT} \ll 1$, which corresponds to the situation close to the Boltzmann limit, the number of particles N_0 in the ground state (ϵ=0) is negligible. As $\epsilon^{\mu/kT}$ increases and becomes close to the order of unity, N_0 can be a significant fraction of the total number of particles N. Under these circumstances, the behaviour of the system is significantly different from the classical one.

We consider the ideal Bose gas of spinless particles (where g = 1). As we have discussed in the previous section, the total number of particles N and the total energy U are expressed as

$$N_e \equiv N - N_0 = (2\pi V/h^3)(2m)^{3/2} \int_0^\infty \epsilon^{1/2} d\epsilon / (z^{-1}e^{\beta\epsilon} - 1) \quad (7.2.1)$$

and

$$U = (2\pi V/h^3)(2m)^{3/2} \int_0^\infty \epsilon^{3/2} d\epsilon / (z^{-1}e^{\beta\epsilon} - 1) \quad (7.2.2)$$

where N_0 is the number of particles in the ground state ($\epsilon = 0$) and N_e those in the excited state ($\epsilon \neq 0$).

Putting $\beta\epsilon = x$, Eqs.(7.2.1) and (7.2.2) reduce to

$$N_e \equiv N - N_0 = 2\pi V (2mkT/h^2)^{3/2} \int_0^\infty x^{1/2} dx/(z^{-1}e^x - 1)) \quad (7.2.3)$$

$$U = 2\pi V(kT)(2mkT/h^2)^{3/2} \int_0^\infty \epsilon^{3/2} d\epsilon / (z^{-1}e^x - 1) \quad (7.2.4)$$

Evaluating the integrals appearing in (7.2.3) and (7.2.4), we get

$$N_e = N - N_0 = (V/\lambda^3)\, g_{3/2}(z) \quad (7.2.5)$$

and

$$U = (3/2)\, kT\, (V/\lambda^3)\, g_{5/2}(z) \quad (7.2.6)$$

where

$$\lambda = (h^2/2\pi mkT)^{1/2} \quad (7.2.7)$$

and

$$g_n(z) = (1/\Gamma(n)) \int_0^\infty [x^{n-1} / (z^{-1}e^x - 1)]\, dx \quad (7.2.8)$$

$\Gamma(n)$ is a gamma function. For small values z, we can expand $(z^{-1}e^x - 1)^{-1}$ in the form

$$1 / (z^{-1}e^x - 1) = ze^{-x}(1 - ze^{-x})^{-1} = \sum_{l=1}^{\infty} z^l e^{-lx}$$

Thus $g_n(z)$ can be evaluated as

$$g_n(z) = (1/\Gamma(n)) \sum_{l=1}^{\infty} z^l \int_0^\infty e^{lx} x^{n-1} dx = \sum_{l=1}^{\infty} (z^l/l^n)$$

$$= z + (z^2/2^n) + (z^3/3^n) + \ldots \quad (7.2.9)$$

For Bose gas, the chemical potential μ is always negative and hence, $z \leq 1$. When the temperature is lowered, z increases from 0 to the maximum value $z = 1$. The maximum value $z = 1$ is reached at a critical temperature T_c. Let us determine this temperature by putting $z = 1$ in (7.2.5). In this case N_e is prectically identical with the total number of particles N. Thus,

$$N = (2\pi mkT_c/h^2)^{3/2} V\xi(3/2) \quad (7.2.10)$$

where

$$g_{3/2}(1) = \xi(3/2) = 1 + (1/2^{3/2}) + (1/3^{3/2}) + \ldots \quad (7.2.11)$$

Here $\xi(l) \equiv \sum_{l=1}^{\infty} 1/n^l$ is the Riemann zeta function. Hence T_c is expressed as

$$T_c = (N/\xi(3/2)V)^{3/2} (h^2/2\pi mk) \quad (7.2.12)$$

For all known Bose gases, T_c corresponds to a very low temperature. Thus for example, for HE^4, we obtain $T_c = 3.13$ K. Though this is a very low temperature, there is still a region $0 \leq T \leq T_c$ where the Bose gases show some specific behaviour.

1. Thermodynamic behaviour of an ideal gas when $T < T_c$

In this temperature range $\mu = 0$ (i.e. $z = 1$) and the number of particles in the excited state will be

$$N_e = N - N_0 = (2\pi mkT/h^2)^{3/2} V\xi(3/2) \quad (7.2.13)$$

Consequently, for a given value of V and T,

$$N > (2\pi mkT/h^2)^{3/2} V\xi(3/2)$$

Then the excited state will receive as many particles as they can hold according to (7.2.13), and rest of them (N_0) will be in the ground state ($\epsilon = 0$). So long as

$$N \leq (2\pi mkT/h^2)^{3/2} V\xi(3/2)$$

practically all the particles in the system are in the excited state ($\epsilon \neq 0$).

From (7.2.10) and (7.2.12), the number of particles with energies $\epsilon \neq 0$ will be

$$N_e = N(T/T_c)^{3/2} \quad (7.2.14)$$

and those with energy $\epsilon = 0$.

$$N_0 = N[1 - (T/T_c)^{3/2}] \quad (7.2.15)$$

Thus, a large number of particles accumulate in the ground state ($\epsilon = 0$). This is the famous phenomenon of Bose Einstein condensation. This differs from the ordinary vapour condensation, which takes place in the ordinary physical space by lowering the temperature, while the Bose-Einstein condensation is purely of a quantum origin.

Accordingly, for $T \leq T_c$, an ideal Bose gas may exist in two phases:

(i) a gaseous phase consisting of N_e particles distributed over the excited state ($\epsilon \neq 0$) and

(ii) a condensed phase consisting of N_0 particles, which occupy the ground state ($\epsilon = 0$).

Figure 7.1 demonstrates the variations of N_e/N and N_0/N with the temperature. At $T = 0$, all the particles of the system occupy the ground state ($\epsilon = 0$), while at $T = T_c$, all the particles are in the excited state ($\epsilon \neq 0$) and no particle will be in the ground state. For $T > T_c$, we have the gaseous phase alone.

Let us now calculate the thermodynamic properties of an ideal Bose gas for $T \leq T_c$.

With the help of (7.2.6) (with z = 1) and (7.2.10) we have

$$U(T) = (3/2)\,(\xi(5/2)/\xi(3/2))NkT\,(T/T_c)^{3/2} \qquad (7.2.16)$$

which leads to

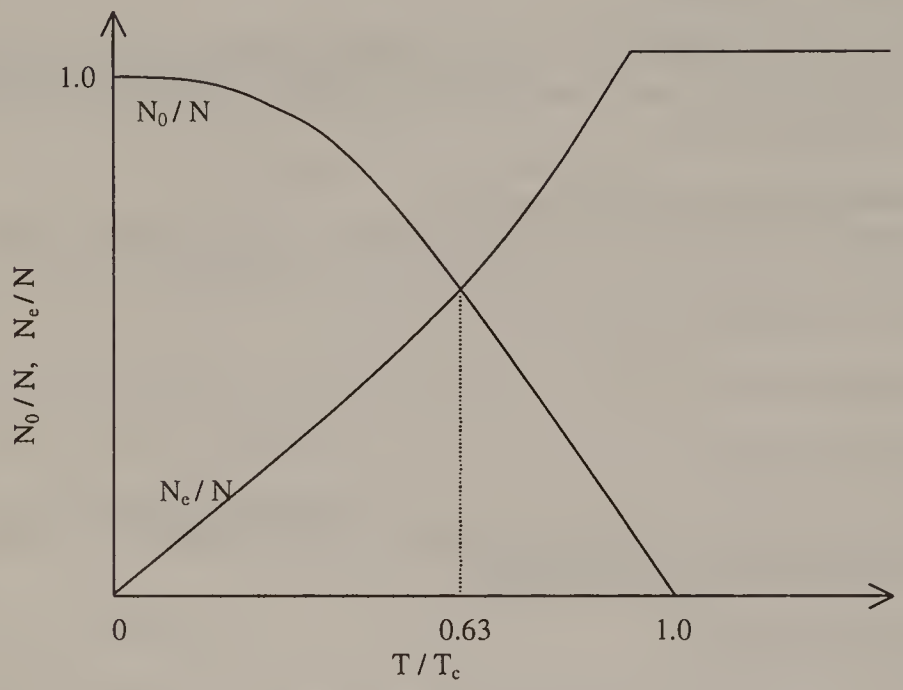


Fig.7.1. Variation of densities of the gaseous phase and condensed phase in an ideal Bose gas as a function of temperature T/T_c

$$U(T) \propto T^{5/2}$$

At the transition point T_c

$$U(T_c) = (3/2)\,(\xi(5/2)/\xi(3/2))NkT_c = 0.5143(3/2NkT_c) \qquad (7.2.17)$$

Thus the energy of an ideal Bose gas at the transition temperature T_c is about one-half of that of an equivalent Boltzmann gas.

The specific heat at constant volume is therefore

$$C_v(T) = (15/4)\,(\xi(5/2)/\xi(3/2))Nk\,(T/T_c)^{3/2}$$

$$= 1.926\ Nk\,(T/T_c)^{3/2} \qquad (7.2.18)$$

which is proportional to $T^{3/2}$. At $T = T_c$, it is

$$C_v(T_c) = 1.926\ Nk \qquad (7.2.19)$$

Integrating the specific heat we get entropy

$$S = \int_0^T (C_v(T)/T)dT = (5/2)\,(\xi(5/2)/\xi(3/2))Nk\,(T/T_c)^{3/2} = (5/3)\,(U/T) \tag{7.2.20}$$

and free energy

$$A = U - ST = -(2/3)U = \Omega \tag{7.2.21}$$

where $\Omega = -PV$ is the thermodynamic potential. Thus for $T < T_c$, the pressure is

$$P(T) = (kT/\lambda^3)\,\xi(5/2) = 0.5134\,(NkT/V)\,(T/T_c)^{3/2} \tag{7.2.22}$$

which is proportional to $T^{5/2}$, and is independent of volume. This is obvious from the fact that particles in the ground state have no momentum and make no contribution to the pressure. With the help of (7.2.10), the pressure at the transition point is given by

$$P(T_c) = (\xi(5/2)/\xi(3/2))\,(NkT_c/V) = 0.5134\,(NkT_c/V) \tag{7.2.23}$$

Thus, the pressure of an ideal Bose gas at T_c is about one half of that of an ideal Boltzmann gas.

2. Thermodynamic behaviour of an ideal gas when $T > T_c$

In this temperature range all the particles of the system remain in the excited state ($\epsilon \neq 0$), and the chemical potential μ is negative (i.e. $z < 1$). Then, energy is given by

$$U(T) = (3/2)\,NkT\,(g_{5/2}(z)/g_{3/2}(z)) \tag{7.2.24}$$

In this case $N_0 = 0$, and from (7.2.5) and (7.2.10), we get

$$g_{3/2}(z) = \xi(3/2)\,(T_c/T)^{3/2} \tag{7.2.25}$$

It can be shown that

$$\begin{aligned} g_{5/2}(z)/g_{3/2}(z) &= 1 - (1/2^{5/2})g_{3/2}(z) - ((2/3^{5/2}) - (1/2^3))(g_{3/2}(z))^2 + \ldots \\ &= 1 - (\xi(3/2)/2^{5/2})\,(T_c/T)^{3/2} - ((2/3^{5/2}) - (1/2^3))\,(\xi(3/2))^2\,(T_c/T)^3 + \ldots \end{aligned} \tag{7.2.26}$$

and hence energy is written as

$$U(T) = (3/2)\,NkT\,[1 - (\xi(3/2)/2^{5/2})\,(T_c/T)^{3/2} - ((2/3^{5/2}) - (1/2^3))\,(\xi(3/2))^2\,(T_c/T)^3 + \ldots] \tag{7.2.27}$$

where the first term is the energy in the Boltzmann limit and the rest are corrections to it. The specific heat is therefore given by

$$C_V(T) = (3/2)\,Nk\,[1 + (\xi(3/2)/2^{7/2})\,(T_c/T)^{3/2} + ((2/3^{5/2}) - (1/2^3))\,(\xi(3/2))^2\,(T_c/T)^3 + \ldots] \tag{7.2.28}$$

giving

$$C_V = (3/2)\,Nk, \qquad \text{when } T = \infty$$

In Fig.7.2, (C_V/Nk) of an ideal Bose gas is represented as a function of T/T_c. Due to the shape of C_V – T curve, the critical temperature T_c, at which the discontinuity appears, is also called T_λ.

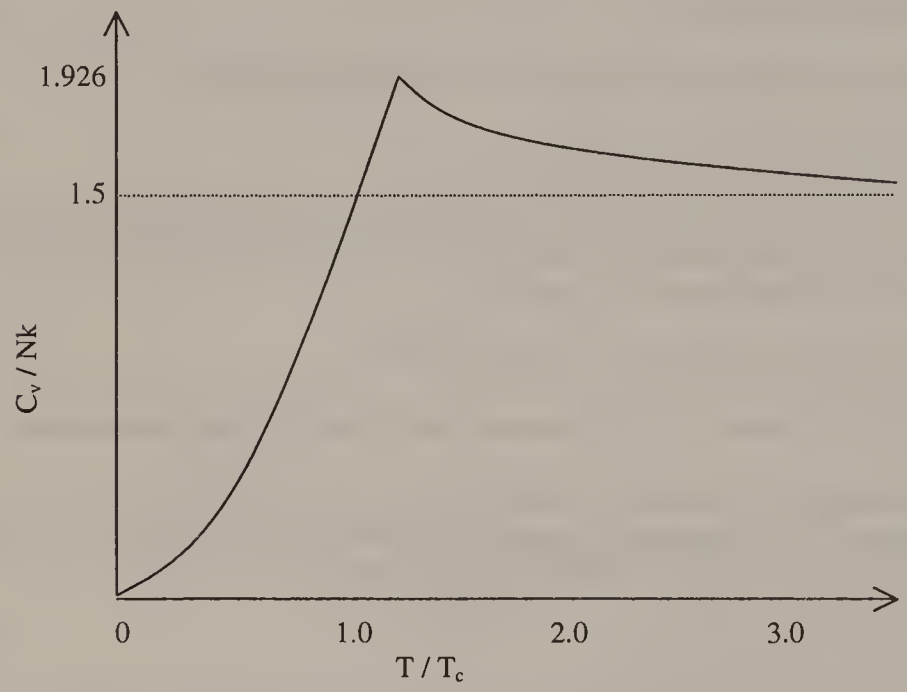


Fig.7.2. The specific heat of an ideal Bose gas as a function of temperature T/T_c.

Using the relation

$$PV = (2/3)\,U$$

the pressure is obtained as

$$P = (NkT/V)\,(g_{5/2}(z)/g_{3/2}(z)) = (NkT/V)\,[1 - (\xi(3/2)/2^{5/2})\,(T_c/T)^{3/2} + \ldots\,] \qquad (7.2.29)$$

The first term is the pressure in the Boltzmann limit and the second is the correction due to the Bose-Einstein statistics, which lowers the value. Thus, when $T \to \infty$, the pressure approaches the classical value NkT/V. The behaviour of pressure of an ideal Bose gas is shown in Fig.7.3.

7.3. Black-Body Radiation: The Photon Gas

The radiation in thermal equilibrium in a box with perfectly reflecting walls may be treated as a 'gas' consisting of photons. According to the quantum theory of electromagnetic radiation, a photon may be regarded as a massless particle of spin $\hbar$ and of definite momentum and energy. It always moves with the velocity of light c.

Since the spin of the photons is unity, this gas obeys Bose-Einstein statistics. Since the atoms can emit, and absorb photons, the number of photons N in the box is a variable and not taken constant as an ordinary gas. Then, the chemical potential μ of the photon is zero.

The distribution of photons among the various quantum states with energies $\epsilon_i = \hbar\omega_i$, where ω_i is the frequency of radiation, in a given volume V at temperature T is given by the Bose-Einstein statistics with $\mu = 0$.

$$n_i = g_i/(\exp(\hbar\omega_i/kT) - 1) \tag{7.3.1}$$

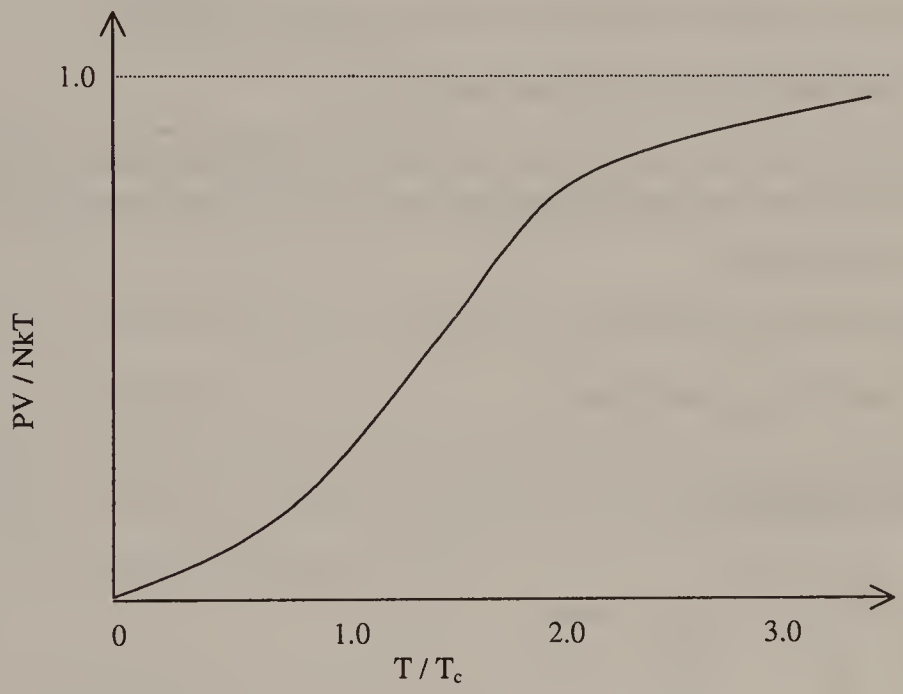


Fig.7.3. The pressure of an ideal Bose gas

So the number of photons having the energies lying between $\hbar\omega$ and $\hbar(\omega+d\omega)$ is given by

$$n(\omega)d\omega = g(\omega)d\omega/(\exp(\hbar\omega/kT) - 1) \tag{7.3.2}$$

Let us consider for simplicity, a cubical box of length L. A photon of frequency ω has momentum $p = \hbar\mathbf{K}$, where $|\mathbf{K}| = \omega/c$. Such a photon corresponds to a plane wave of electromagnetic radiation. The number of quantum states for photons in a box of volume $V = L^3$ in the momentum range p and p + dp is

$$g(p)dp = (4\pi V/(2\pi\hbar)^3)\, p^2 dp \tag{7.3.3}$$

Using the relation $|\mathbf{p}| = \hbar\omega/c$, the number of quantum states with the frequency range ω and $\omega+d\omega$ is obtained as

$$g(\omega)d\omega = (4\pi V/(2\pi\hbar)^3)\,(\hbar\omega/c)^2\,(\hbar d\omega/c) = (V/2\pi^2c^3)\,\omega^2\, d\omega \tag{7.3.4}$$

Taking the two possible polarizations for photons, the number of quantum states in the case of photons is twice as many states as (7.3.4), i.e.

$$g(\omega)d\omega = (V/\pi^2c^3)\,\omega^2\,d\omega \tag{7.3.5}$$

Then the number of photons in the frequency range ω and $\omega+d\omega$ is obtained from (7.3.2) and (7.3.5)

$$n(\omega)d\omega = (V/\pi^2c^3)\,(\omega^2 d\omega/(\exp(\hbar\omega/kT) - 1)) \tag{7.3.6}$$

Hence the energy density of radiation in the frequency range ω and $\omega+d\omega$ is given by

$$\rho(\omega)d\omega = \hbar\omega n(\omega)d\omega/V = (\hbar/\pi^2c^3)\,(\omega^3 d\omega/(\exp(\hbar\omega/kT) - 1) \tag{7.3.7}$$

This equation is correct for radiation in equilibrium with matter. It is the famous Planck's radiation law.

From Planck's formula, we can obtain Rayleigh-Jeans formula for low frequencies, i.e. $\hbar\omega/kT \ll 1$:

$$\rho(\omega)d\omega = (kT/\pi^2c^3)\,\omega^2 d\omega \tag{7.3.8}$$

and Wien's empirical formula at high frequencies, i.e $\hbar\omega/kT \gg 1$:

$$\rho(\omega)d\omega = (\hbar/\pi^2c^3)\exp(-\hbar\omega/kT)\,\omega^2 d\omega \tag{7.3.9}$$

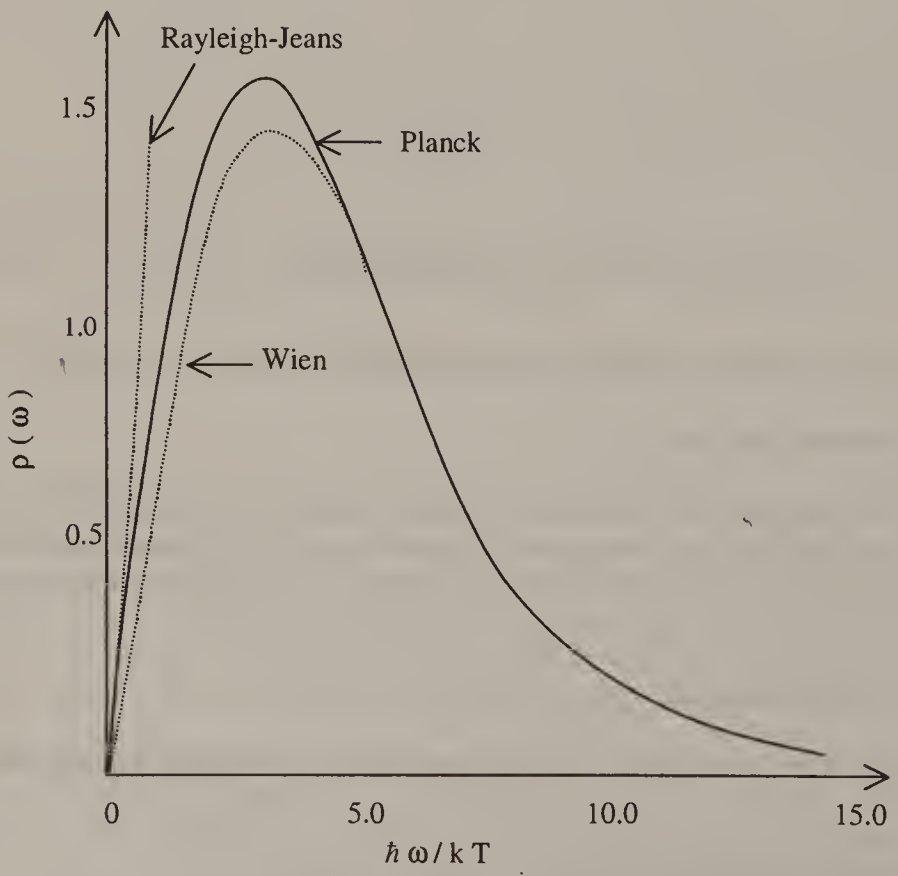


Fig. 7.4. Distribution of energy density in the black body radiation

These are shown in Fig.7.4. We note the areas under the Planck and Wien curves are $\pi^4/15$ 6.49 and 6.0, respectively. However, the Rayleigh-Jeans curve covers no areas, as it continuously increases with frequency.
The total energy density in the radiation cavity is obtained by integrating with respect to ω

$$u = \int_0^\infty \rho(\omega)d\omega = (\hbar/\pi^2c^3)\int_0^\infty \omega^3 d\omega/(\exp(\hbar\omega/kT) - 1)$$

$$= ((kT)^4/\pi^2c^3\hbar^3)\int_0^\infty x^3dx/(e^x - 1) \qquad (7.3.10)$$

where $\hbar\omega/kT = x$. The integral is evaluated as

$$\int_0^\infty x^3dx/(e^x - 1) = \sum_{l=1}^\infty \int_0^\infty e^{-lx}x^3dx = \Gamma(4)\sum_{l=1}^\infty (1/l^4) = \pi^4/15$$

and hence (7.3.10) can be written as

$$u = \pi^2(kT)^4/15c^3\hbar^3 \qquad (7.3.11)$$

If there is a small opening in the walls of the cavity, then radiation will escape from the cavity with velocity c. The amount of energy radiated per second per unit area of the opening is

$$E = (1/4)\,uc = (\pi^2k^4/60\hbar^3c^2)T^4 = \sigma T^4 \qquad (7.3.12)$$

where

$$\sigma = \pi^2k^4/60\hbar^3c^2 \qquad (7.3.13)$$

Equation (7.3.12) is the Stefan-Boltzmann law of the black-body radiation, σ being Stefan's Constant. This law was deduced from experimental observation by Stefan. Later Boltzmann derived it from the thermodynamic considerations.

The specific heat per unit volume is

$$C_V = (\partial u/\partial T)_V = (4\pi^2k^4/15C^3\hbar^3)\,T^3 \qquad (7.3.14)$$

This specific heat is not bounded as $T \to \infty$, because the number of photons in the cavity is not bounded.

7.4. Liquid He^4

Helium has two isotopes He^3 and He^4. He^3 has spin ½, obeying the Fermi Dirac statistics, whereas He^4 has spin zero, obeying the Bose- Einstein statistics. A remarkable property of the two helium isotopes He^3 and He^4 is that they remain liquids, probably down to absolute zero of temperature. However, the two liquid helium have some significantly different physical properties. The difference is due to the fact that the constituent atoms of these liquids obey different statistics.

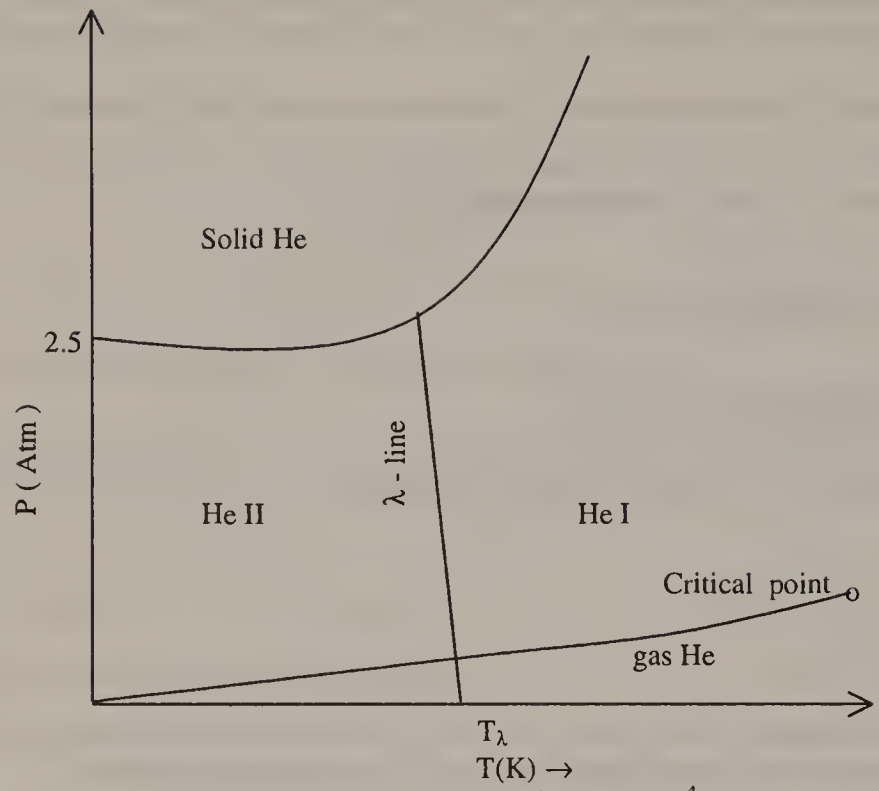


Fig.7.5. The phase diagram for liquid He^4 (not in scale)

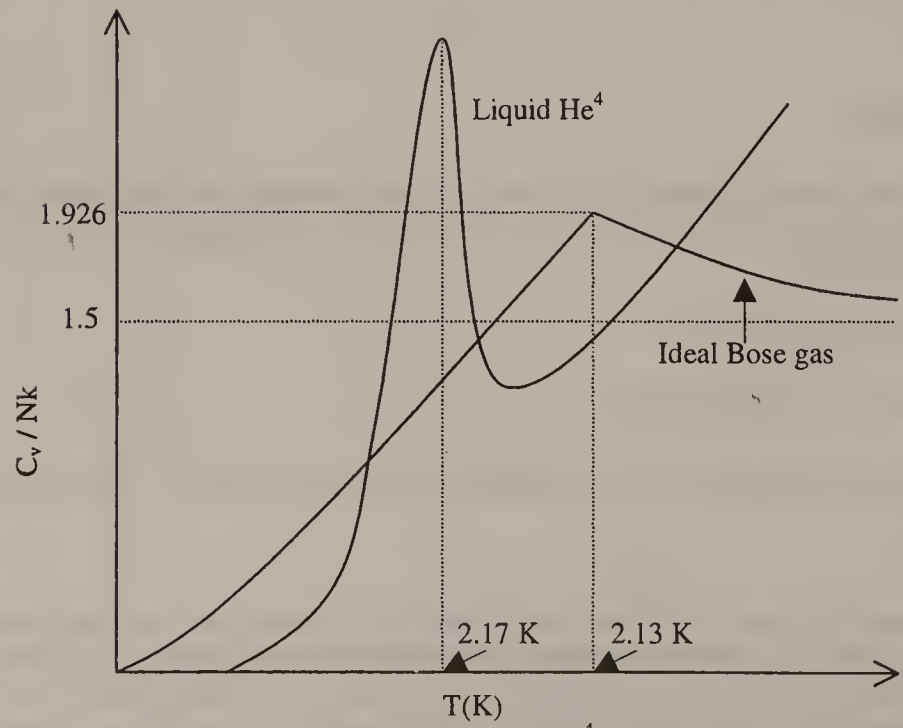


Fig.7.6. Experimental specific heat C_V/Nk of liquid He^4 is compared with the values of specific heat for an ideal boson gas (not in scale).

The phase diagrams of He^4 is shown in Fig.7.5. A peculiar property of He^4 is that it has two liquid phases HeI and HeII. The transition from the liquid HeI to the liquid HeII is called the λ-transition. No such transition has been found in He^3. The transition from HeI to HeII is accompanied by an anomalous of the heat capacity, which is at 2.17 K, as shown in Fig.7.6. Due to the shape of the specific heat curve, this point is called the λ-point. The λ-transition is believed to be related to the Bose-Einstein condensation.

There are two main reasons for the fluidity of helium even at very low temperatures:

(i) weak interaction

(ii) small atomic mass

Helium has a large zero point energy but weak molecular interaction, so that it becomes impossible to localise the atoms at well defined lattice sites. Therefore, helium does not solidify, but remains in the liquid state. Matter composed of other noble elements, like Argon, solidifies at a very low temperature because of its smaller zero-point energy, and hydrogen, although lighter than helium, solidifies because of the stronger molecular interaction. The liquid helium is unique in nature, which remain liquid under ordinary pressure at absolute zero. This properties can be explained in terms of the concept of quantum mechanics. Liquid helium is known as 'quantum liquid'.

Liquid HeI behaves as a fairly normal liquid. On the other hand, liquid HeII has some strange properties. For example, liquid HeII has practically zero entropy and zero viscosity and flows without resistance through fine capillary tubes. Another interesting property of the liquid HeII is that heat propagates like a wave with a definite velocity. This is known as second sound.

These peculiar properties of HeII can be explained by the two fluid theory of Tisza. According to this theory, the liquid HeII is assumed to be a mixture of two fluids- a normal fluid and a super fluid. The normal fluid behaves as an ordinary liquid, and the super fluid has zero entropy, zero viscosity, and flows without resistance through capillary tubes. The relative amount of normal and super fluids depends on the temperature; the percentage of the super fluid component increases from zero at T_λ to unity at the absolute zero of temperature. However, the two fluid theory does not provide a complete understanding of liquid HeII as it has no molecular basis.

7.5. Ideal Bose Gas Model of Liquid He^4

Let us now discuss the molecular theory to explain the behaviour of liquid He^4.

Liquid helium has a weak intermolecular interaction. The helium atoms may be regarded roughly as moving freely in a constant attractive central potential. London assumed that liquid He^4 is an ideal boson gas, obeying Bose-Einstein statistics.

Treating the liquid He^4 as spinless ideal Bose gas, the critical temperature T_c is

$$T_c = (N/2.612\ V)^{2/3} (h^2/2\pi mk)$$

Using the following data for liquid He^4

$$m = 6.65 \times 10^{-27}\ kg$$

$$V = 27 \times 10^{-6}\ m^3$$

so that

$$N/V = 2.2 \times 10^{28}\ m^{-3}$$

we find that the critical temperature $T_c = 3.13$ K, which is not very far from the experimental value of $T_\lambda = 2.17$ K. In the region $0 \leq T \leq T_c$, the boson gas shows some specific behaviour.

According to the ideal Bose gas model, for $T \leq T_c$, the liquid He^4 may be considered as a mixture of a gaseous phase of N_e particles distributed over the excited states ($\epsilon \neq 0$), and a condensed phase of N_0 particles which occupy the ground state ($\epsilon = 0$). Accumulation of a large number of particles in the ground state is responsible for the Bose-Einstein condensation, and corresponds to the superfluid component of liquid HeII. On the other hand, the particles in the excited states corresponds to the normal component of liquid HeII. Thus, for $0 \leq T \leq T_c$, we have

$$N_e/N = (T/T_c)^{3/2} \tag{7.5.2a}$$

and

$$N_0/N = [1 - (T/T_c)^{3/2}] \tag{7.5.2b}$$

from which it is clear that at $T = 0$, we have only superfluid component, while at $T = T_c$, we have only normal fluid component. For $T > T_c$, we have normal fluid alone.

Let us now calculate the thermodynamic properties of liquid He^4. The energy is given by

$$U(T) = (3/2)\,(\xi(5/2)/\xi(3/2))NkT\,(T/T_c)^{3/2} \qquad \text{for } T \leq T_c$$

$$= (3/2)NkT\,[1 - (\xi(3/2)/\xi(5/2))\,(T_c/T)^{3/2} - ((2/3^{5/2}) - (1/2^3))\,(\xi(3/2))^2\,(T_c/T)^3$$

$$+ \ldots\,] \qquad \text{for } T > T_c \tag{7.5.3}$$

Then, the specific heat at constant volume is

$$C_V(T) = (15/4)\,(\xi(5/2)/\xi(3/2))Nk\,(T/T_c)^{3/2} \qquad \text{for } T \leq T_c \tag{7.5.4}$$

$$= (3/2)NkT\,[1 - (\xi(3/2)/2^{7/2})\,(T_c/T)^{3/2} + 2((2/3^{5/2}) - (1/2^3))\,(\xi(3/2))^2\,(T_c/T)^3$$

$$+ \ldots\,] \qquad \text{for } T > T_c \tag{7.5.5}$$

Thus from (7.5.4) we find that

$$C_V \propto T^{3/2} \qquad \text{for} \qquad T < T_c$$

leading to

$$C_V \to 0 \qquad \text{when} \quad T \to 0$$

and

$$C_V = 1.926Nk \quad \text{at} \quad T = T_c$$

and from (7.5.5) we see that

$$C_V = (3/2)Nk \quad \text{at} \quad T \to \infty$$

The values of the specific heat C_V for an ideal Bose gas are shown in Fig.7.6 along with the experimental values for liquid He^4. The specific heat of the ideal Bose gas model resembles qualitatively with that of liquid He^4. However, the quantitative differences are very significant.

Experimentally it is found that the specific heat of liquid HeII below o.6 K obeys the Debye T^3, whereas (7.5.4) provides that for the ideal Bose gas below T_c, $C_V \propto T^{3/2}$. The value of C_V at T_c for the ideal Bose gas is 1.926 Nk, which is much smaller than that of liquid He^4 near T_λ. In addition, T_c of the ideal Bose gas model is greater than T_λ of the liquid He^4.

The interactions among He^4 atoms are small but not negligible. For this reason, the ideal Bose gas model is inadequate to explain many properties of liquid HeII. However, this theory has been used as a guide to the correct theory and a better understanding of the problem.

7.6. Landau Theory of Liquid HeII

In Sec.7.5, the ideal Bose gas model has been used to explain the thermodynamic behaviour of liquid HeII. This model predicts that $C_V \propto T^{3/2}$, while experimentally the specific heat C_V of the liquid HeII obeys the T^3 law as $T \to 0$. Such a behaviour is characteristic of a gas of phonons, which is explained reasonably well by a theory developed by Landau (1941, 1947).

According to Landau, liquid HeII is a background fluid (superfluid) in which excitations move. At absolute zero of temperature, the entire liquid is in its ground state (superfluid phase) with internal energy $U = U_0$. When the temperature is raised, the system moves into excited states, the number of which increases with temperature. Any low excited state of a system can be regarded in quantum mechanics as an assembly of elementary excitations which behave as quasi-particles. The quasi-particles have definite energies and momenta, and move in the volume occupied by the system. At very low temperatures, the number of elementary excitations is sufficiently small, so they do not interact with one another. Hence the assembly of these excitations may be regarded as an ideal gas. The energy levels of such quantum states is

$$U = U_0 + \sum_{\mathbf{p}} \epsilon(\mathbf{P}) n(\mathbf{P}) \tag{7.6.1}$$

where $\epsilon(\mathbf{P})$ is the energy of an elementary excitation of momentum $\mathbf{P}$, and $\{n(\mathbf{P})\}$ is a set of occupation numbers. It is assumed that the elementary excitations are bosons, so that $n(\mathbf{P}) = 0, 1, 2, \ldots$. Landau assumed two types of excitations. At low momentum, the excitations are the phonons or quantized sound waves with energy

$$\epsilon(\mathbf{P}) = cp \tag{7.6.2}$$

where p is the momentum and c is the velocity of sound. As the momentum increases, we get another type of excitation-quantized classical vortex motion, called rotons, whose energy is represented by

$$\epsilon(\mathbf{P}) = \Delta + ((p - p_0)^2/2\mu) \tag{7.6.3}$$

where $\Delta = \epsilon(p_0)$ and μ is the effective mass.

If the number of phonons and rotons is not very large, the liquid helium can be regarded as a mixture of two ideal gases – a phonon gas and a roton gas. These two excitations are assumed to be two parts of one and the same excitation energy-momentum curve $\epsilon(P)$ as shown in Fig.7.7. The energy $\epsilon(P)$ first rises linearly, reaching a maximum, then falls to minimum at p_0 and rises again. In thermal equilibrium, the regions near the minima of $\epsilon(P)$ are of particular importance.

Both phonons and rotons contribute to the thermodynamic properties of liquid HeII. However, their relative contributions depend on the temperature. At sufficiently low temperatures below 0.5 K, the contribution of phonons to the thermodynamic behaviour of the liquid is predominating while above 1 K, the roton contribution is relatively more important. Between 0.5 K and 1 K, the thermodynamic behaviour of the liquid is governed by both phonons and rotons.

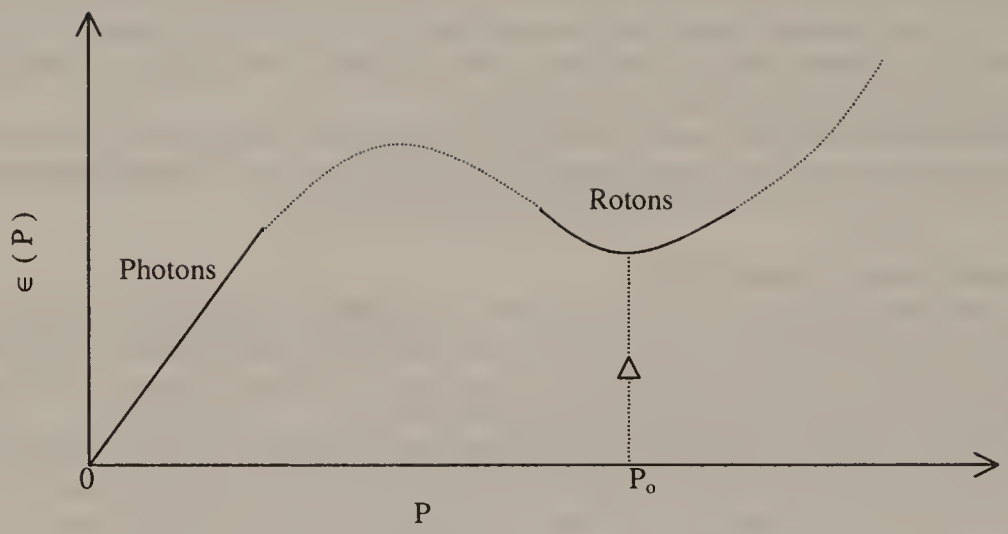


Fig.7.7. Energy spectrum of elementary excitations in Landau's theory

We suppose that the excitations are noninteracting bosons whose total number is not conserved. The mean occupation number <n(p)> is

$$<n(P)> = (1/ e^{\beta \in (P)} - 1) \tag{7.6.4}$$

where $\beta = 1/kT$. The internal energy of the liquid helium is

$$U = U_0 + \sum_p \in (P) <n(P)>$$

$$= U_0 + (4\pi V/h^3) \int_0^\infty (\in (P)/(e^{\beta \in (P)} - 1))\, p^2 dp \tag{7.6.5}$$

where V is the volume occupied by the liquid. Using (7.6.2) and (7.6.3) we can write the internal energy in the form

$$U = U_0 + U_{ph} + U_{rot} \tag{7.6.6}$$

and the specific heat at constant volume is

$$C_V = (\partial U/\partial T)_V = (C_V)_{ph} + (C_V)_{rot} \tag{7.6.7}$$

Thus at sufficiently low temperatures, the specific heat of liquid HeII consists of two parts- phonons and roton.

Let us first consider the phonon contribution. The number of phonons is given by

$$N_{ph} = (4\pi V/h^3) \int_0^\infty (p^2/(e^{\beta cp} - 1))\, dp = (4\pi V/h^3 c^3)\, (kT)^3 \int_0^\infty (x^2/ (e^x - 1))\, dx$$

where we have put $\beta cp = x$. The integral can be evaluated to give

$$N_{ph} = (8\pi\xi(3)V/h^3c^3)\,(kT)^3 \tag{7.6.8}$$

where $\xi(n)$ is Riemann zeta function. The internal energy due to phonons can be written as

$$U_{ph} = (4\pi V/h^3)\int_0^\infty (cp^3/(e^{\beta cp}-1))\,dp = (4\pi V/h^3c^3)\,(kT)^4\int_0^\infty (x^3/(e^x-1))\,dx$$

This integral can be evaluated to give as

$$U_{ph} = (24\pi\xi(4)V/h^3c^3)\,(kT)^4 = 3\,(\xi(4)/\xi(3))\,N_{ph}kT \tag{7.6.9}$$

Then the phonon contribution to the specific heat is

$$(C_v)_{ph} = k(96\pi\xi(4)V/h^3c^3)\,(kT)^3 = Nk\,(16\pi^5 v/15h^3c^3)\,(kT)^3 \tag{7.6.10}$$

where $v = V/N$.

Alternatively (7.6.9) can be written as

$$(C_v)_{ph} = (12\xi(4)/\xi(3))\,N_{ph}k \tag{7.6.11}$$

Clearly as $T\to 0$, $(C_V)_{ph} \to 0$.

Next we consider the contribution of the roton part. For the roton part, the energy $\in(P)$ is given by (7.6.3). At the temperature of interest (viz. $T \le 2K$), $e^{\Delta/kT}$ is considerably larger than unity and so we can neglect unity in comparison to $e^{-\beta\in(P)}$ in (7.6.4). Then the number of rotons is given by

$$N_{rot} = (4\pi V/h^3)\,e^{-\Delta/kT}\int_0^\infty \exp\left[-((p-p_0)^2/2\mu kT)\right]p^2dp$$

and the internal energy of the roton part is

$$U_{rot} = (4\pi V/h^3)e^{-\Delta/kT}\int_0^\infty \exp[-((p-p_0)^2/2\mu kT)]\,[\Delta + ((p-p_0)^2/2\mu)]p^2dp$$

Putting $(p-p_0)/(2\mu kT)^{1/2} = X$ and since $2\mu kT/p_0^2 \ll 1$, the number of rotons is evaluated as

$$N_{rot} = (4\pi V/h^3)e^{-\Delta/kT}\,p_0^2\,(2\mu kT)^{1/2}\int_0^\infty \exp(-X^2)\,dX$$

$$= (2\pi V/h^3)e^{-\Delta/kT}\,p_0^2\,(2\pi kT)^{1/2} \tag{7.6.12}$$

The internal energy of the roton part is evaluated as

$$U_{rot} = (4\pi V/h^3)e^{-\Delta/kT}\,p_0^2\,(2\mu kT)^{1/2}\int_0^\infty \exp(-X^2)\,[\Delta + kTX^2]dX$$

$$= (2\pi V/h^3)e^{-\Delta/kT}\,p_0^2\,(2\pi\mu kT)^{1/2}\,[\Delta + (1/2)kT] \tag{7.6.13}$$

From (7.6.12) and (7.6.13), we get

$$U_{rot} = N_{rot}[\Delta + (1/2)kT] \tag{7.6.14}$$

The specific heat of the roton part is

$$(C_v)_{rot} = (\partial U_{rot}/\partial T)_V$$

$$= (2\pi V/h^3)e^{-\Delta/kT} p_0^2 (2\pi\mu kT)^{1/2} k [(3/4) + (\Delta/kT) + (\Delta/kT)^2]$$

$$= N_{rot} k [(3/4) + (\Delta/kT) + (\Delta/kT)^2] \tag{7.6.15}$$

It is clear from these results that as $T \to 0$, $N_{rot} \to 0$ and $(C_v)_{rot} \to 0$.

Substituting (7.6.11) and (7.6.15) in (7.6.7), the specific heat at constant volume is given by

$$C_v = Nk[(12\xi(4)/\xi(3))(N_{ph}/N) + \{(3/4) + (\Delta/kT) + (\Delta/kT)^2\}(N_{rot}/N)] \tag{7.6.16}$$

Thermodynamic properties are in excellent agreement with theory if we take

$$c = 240 \text{ m/s}; \qquad \Delta/k = 9.6 \text{ K}; \qquad \rho_0/\hbar = 2.0\text{A}^{-1}; \qquad \mu = 0.77 \text{ m}$$

where m is the atomic mass of helium.
At sufficiently low temperature $(C_v)_{rot}$ is found to be smaller than $(C_v)_{ph}$. However at temperature $T \leq 1.2$ K, the roton gas plays a dominant role in the specific heat.

Let us now determine the mass density ρ_n of the normal component, consisting of phonons and rotons in thermal equilibrium where

$$\rho_n = \rho_n^{ph} + \rho_n^{rot} \tag{7.6.17}$$

We consider the phonon gas and the roton gas in mass motion separately. Since the total number of quasi-particles (phonons or rotons) in the system is indefinite, for evaluating the density ρ_n we calculate the momentum **P** of the gas of quasi-particles, each of which has a small constant drift velocity **u**. Let the z-axis be the direction of the mass motion, then each quasi particle will have a component of momentum of p cosθ in the z-axis. So the energy of each quasi-particle will be

$$\epsilon(\mathbf{p}) = \epsilon_0 + up\cos\theta = \epsilon_0 + \mathbf{u.p} \tag{7.6.18}$$

where ϵ_0 is the energy of excitation of a quasi-particle. Under this condition, the mean occupation number of the quasi-particle will be

$$\langle n(p)\rangle = 1/(\exp[\beta(\epsilon_0 + \mathbf{u.p})] - 1) \tag{7.6.19}$$

The total momentum <p> of the gas of quasi-particles will be simply the z-component of the momentum. It can be expressed as

$$P = P_z = \sum_p \langle n(p) \rangle p_z = (2\pi V/h^3) \int_0^\infty \int_0^\pi \langle n(\mathbf{p}) \rangle p^3 \, dp \cos\theta \sin\theta \, d\theta \tag{7.6.20}$$

Since u is small, we can expand $\langle n(\mathbf{p}) \rangle$ as

$$\langle n(\mathbf{p}) \rangle \quad (1/(\exp(\beta\epsilon_0) - 1)) + (\exp(\beta\epsilon_0)/(\exp(\beta\epsilon_0) - 1)) \, \beta up \cos\theta \tag{7.6.21}$$

where higher order terms are neglected.
Substituting (7.6.21) in (7.6.20), we get

$$P = (2\pi V/h^3) \int_0^\infty \int_0^\pi (p^3 \, dp / (\exp(\beta\epsilon_0) - 1)) \cos\theta \sin\theta \, d\theta$$

$$+ (2\pi V\beta u/h^3) \int_0^\infty \int_0^\pi (\exp(\beta\epsilon_0) p^4 dp/(\exp(\beta\epsilon_0) - 1)^2) \cos^2\theta \sin\theta d\theta \tag{7.6.22}$$

when integrating over θ, the first integral vanishes. Thus, we get

$$P = (4\pi V\beta u/h^3) \int_0^\infty (\exp(\beta\epsilon_0)/(\exp(\beta\epsilon_0) - 1)^2) p^4 dp \tag{7.6.23}$$

For phonons, $\epsilon_0 = cp$. Substituting this value in (7.6.23) and integrating by parts, we get

$$P_{ph} = (16\pi V/3h^3c)u \int_0^\infty (p^3 dp / (e^{\beta cp} - 1) = (4/3) (U_{ph}/c^2)u) \tag{7.6.24}$$

The inertial mass of the phonon gas is

$$m_{ph} = P_{ph} / u$$

and hence the corresponding mass density ρ_n^{ph} is given by

$$\rho_n^{ph} = (P_{ph}/uV) = (4/3c^2) (U_{ph}/V) = (16\pi^5/45h^3c^5) (kT)^4 \tag{7.6.25}$$

At the lowest temperature, the energy density is found to be

$$U_{ph}/V = 5 \times 10^4 \rho T^4 \text{ erg/cm}^3$$

where ρ is the density of the liquid HeII and the velovity of the sound wave is

$$C = 240 \text{ m/s}$$

then, the phonon density is given by

$$\rho_n^{ph}/\rho = 1.22 \times 10^{-4} \, T^4 \tag{7.6.26}$$

For rotons, $\langle n(\epsilon_0)\rangle$ $\exp(-\beta\epsilon_0)$ and (7.6.23) can be expressed as

$$P_{rot} \quad (4\pi V/3h^3)\beta u \int_0^\infty \exp(-\beta\epsilon_0)\, p^4 dp \tag{7.6.27}$$

substituting (7.6.3), it can be expressed

$$P_{rot} = (4\pi V/h^3)u p_0^4 e^{-\Delta/kT} (2\mu/kT)^{1/2} \int_0^\infty \exp(-X^2)\, dX$$

$$= (2\pi V/3h^3)u p_0^4 e^{-\Delta/kT} (2\pi\mu/kT)^{1/2} \tag{7.6.28}$$

and roton mass density

$$\rho_n^{rot} = (P_{rot}/uV) = (2\pi p_0^4/3h^3)(2\pi\mu/kT)^{1/2} e^{-\Delta/kT} = (p_0^2/3kT)(N_{rot}/V) \tag{7.6.29}$$

or $$\rho_n^{rot}/\rho = (2\pi p_0^4/3\rho h^3)(2\pi\mu/kT)^{1/2} e^{-\Delta/kT} \tag{7.6.30}$$

Thus the fraction ρ_{rot}/ρ decreases exponentially with temperature and becomes negligible at the lowest temperatures. Figure 7.8 shows the variation of the two excitations with temperature.

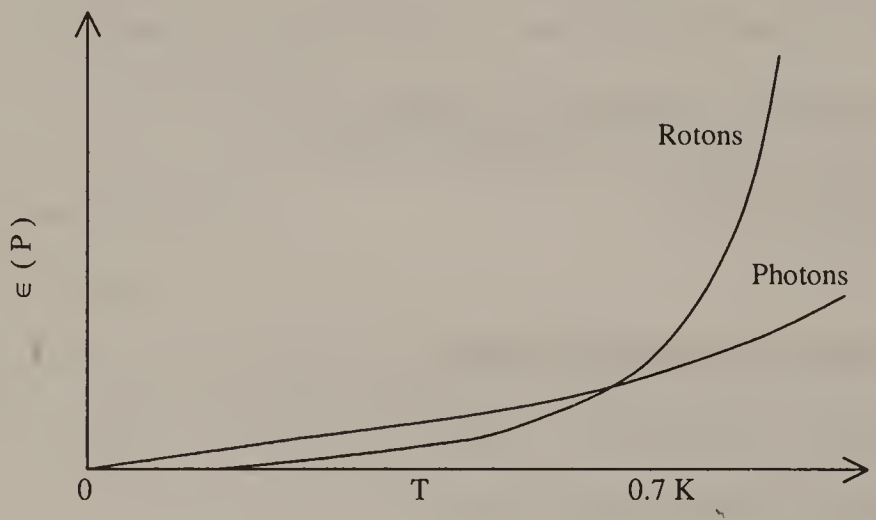


Fig.7.8. The phonon and roton contributions to the normal component of liquid HeII as a functions of temperature.

The Landau theory predicts the ratio of the normal component of the liquid HeII:

$$\rho_n/\rho = (\rho_n^{ph}/\rho) + (\rho_n^{rot}/\rho) \tag{7.6.31}$$

and the ratio of the superfluid component:

$$\rho_s/\rho = 1 - (\rho_n/\rho) \tag{7.6.32}$$

This result gives a very accurate description of the experimental data of ρ_n.

When the ratio ρ_n/ρ is put equal to unity, the resulting temperature will be the critical temperature T_c, at which the superfluid component disappears. The result gives $T_c = 2.3$ K, which is in good agreement with experimental value. However, we have not considered the roton-roton interaction in the present theory, which is expected to be important at high temperature due to the presence of exceedingly large number of excitations.

7.7. Feynman's Theory of Liquid HeII

Feyman (1954) has made an interesting extension of Landau's theory for liquid HeII, which thrown more light on the nature of the elementary excitations. Landau has tried to give some justification for the energy spectrum of these excitations with the help of quantum hydrodynamics. However, this is not a completely detailed atomic approach.

Let the Hamiltonian of liquid He^4 be

$$\hat{H} = -(\hbar^2/2m) \sum_{i=1}^{N} \nabla_i^2 + \sum_{i<j} u(r_{ij}) \tag{7.7.1}$$

where $u(r_{ij})$ is the pair potential between the atoms i and j, and m is the mass of a He^4 atom. In order to achieve a more fundamental formulation, we should regorously solve the Schrodinger equation for the system

$$\hat{H}\Psi = E\Psi \tag{7.7.2}$$

But this is clearly a fantastic impossibility as the system is an aggregate of roughly 10^{22} particles. Feynman has developed a theoretical scheme, which can throw considerably more light in predicting the characteristics of the wave function.

Let $\Psi_0(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ be the ground state wave function, then

$$\hat{H}\Psi_0 = E_0\Psi_0 \tag{7.7.3}$$

where E_0 is the ground state energy eigenvalue. Ψ_0 is real and positive, and must be a symmetric function of the coordinates $\mathbf{r}_1, \ldots, \mathbf{r}_N$.

We now consider the low-energy excited states of the liquid HeII. The wave function Ψ for an excited state should contain Ψ_0. The function Ψ must be orthogonal to Ψ_0 and must remain symmetric with respect to interchange of any pair of coordinates.

Feynman assumes that the wave function for an excited state of the liquid He^4 is of the form

$$\Psi = F\Psi_0 \tag{7.7.4}$$

with

$$F = \sum_{i=1}^{N} f(\mathbf{r}_i) \tag{7.7.4'}$$

where $f(\mathbf{r}_i)$ is some function of position $\mathbf{r}_i$ and the summation is taken over all atoms. The function f(r) can be determined by minimising the energy of the state Ψ. The energy of the excited state can be estimated from the relation

$$\epsilon = \int \Psi^*(\hat{H} - E_0)\,\Psi d\tau \int \Psi^*\Psi\, d\tau = \varepsilon/J \tag{7.7.5}$$

where

$$\varepsilon = \int \Psi^* (\hat{H} - E_0)\, \Psi d\tau \tag{7.7.6}$$

$$J = \int \Psi^* \Psi \, d\tau \tag{7.7.7}$$

Here, $d\tau = \prod_{i=1}^{N} dr_i$ is the volume element.

The condition for minimum energy is

$$\delta \epsilon = 0 \tag{7.7.8}$$

which gives, when (7.7.5) is used

$$\delta \varepsilon - \epsilon \delta J = 0 \tag{7.7.9}$$

This relation can be used to obtain an expression for the energy ϵ of the excited state.

Using the relation

$$\sum_i \nabla_i^2 (F\Psi_0) = \sum_i [\Psi_0 \nabla_i^2 F + 2\nabla_i F . \nabla_i \Psi_0 + F \nabla_i^2 \Psi_0] \tag{7.7.10}$$

we can write

$$(\hat{H} - E_0)\Psi = -(\hbar^2/2m) \sum_{i=1}^{N} [\Psi_0 \nabla_i^2 F + 2\nabla_i F . \nabla_i \Psi_0]$$

$$= -(\hbar^2/2m\Psi_0) \sum_{i=1}^{N} \nabla_i . [\Psi_i^2 \nabla_i F] \tag{7.7.11}$$

Using this value, we can evaluate the function ε as

$$\varepsilon = \int \Psi^* (\hat{H} - E_0)\, \Psi dr$$

$$= -(\hbar^2/2m) \sum_{i=1}^{N} \int F^* \nabla_i . [\Psi_0^2 \nabla_i F] \prod_{i=1}^{N} dr_i$$

$$= (\hbar^2/2m) \sum_{i=1}^{N} \int [\Psi_0^2 \nabla_i F^* . \nabla_i F - \nabla_i . (\Psi_0^2 F^* \nabla_i F)] \prod_{i=1}^{N} dr_i \tag{7.7.12}$$

The contribution of the second integral of (7.7.12) is zero when the wave function vanishes at the boundary of the configuration space. Only the first integral will contribute to ε.
Substituting (7.7.4') we obtain an expression for

$$\varepsilon = (\hbar^2 N/2m) \int \Psi_0^2 \nabla_1 f^*(r_1).\nabla_1 f(r_1) \prod_{i=1}^{N} dr_i$$

$$= (\hbar^2 \rho/2m) \int \nabla_1 f^*(r_1).\nabla_1 f(r_1)\, dr_i \qquad (7.7.13)$$

where

$$n_N(r_1) = N \int \Psi_0^2 \prod_{i=2}^{N} dr_i \qquad (7.7.14)$$

is the one-particle distribution function, and for uniform liquid, $n_N(r_1) = \rho$, where $\rho = N/V$ is the number density.

Next, we calculate

$$J = \int \Psi^* \Psi \prod_{i=1}^{N} dr_i = \int \Psi_0^2 F^* F \prod_{i=1}^{N} dr_i$$

$$= \sum_{i=1}^{N} \sum_{j=1}^{N} \int \Psi_0^2 f^*(r_i) f(r_j) \prod_{i=1}^{N} dr_i$$

$$= N \int \Psi_0^2 |f(r_1)|^2 \prod_{i=1}^{N} dr_i + N(N-1) \int \Psi_0^2 f^*(r_1) f(r_2) \prod_{i=1}^{N} dr_i$$

$$= \rho \int |f(r_1)|^2 dr_1 + \int n_N(r_1,r_2) f^*(r_1) f(r_2)\, dr_1\, dr_2 \qquad (7.7.15)$$

where

$$n_N(r_1,r_2) = N(N-1) \int \Psi_0^2 \prod_{i=3}^{N} dr_i \qquad (7.7.16)$$

is the two-particle distribution function.

We now introduce the pair correlation function defined by

$$\rho D(r_1,r_2) = \sum_{i=1}^{N} \sum_{j=1}^{N} \int \prod_{i=1}^{N} dr_i' \, \delta(r_i' - r_1)\, \delta(r_j' - r_2)\, \Psi_0^2$$

$$= \int dr_1' \, \delta(r_1' - r_1)\, \delta(r_1' - r_2)\, n_N(r_1') + \int dr_1' \, dr_2' \, \delta(r_1' - r_2)\, \delta(r_2' - r_2)\, n_N(r_1', r_2)$$

$$= \rho\, \delta(r_1 - r_2) - n_N(r_1', r_2) \qquad (7.7.17)$$

where $D(r_1,r_2)$ is the probability density of finding a particle at r_1 where second particle is at r_2 in the ground state of the system. It depends on $r_{12} = |r_2 - r_1|$
Then J can be expressed as

$$J = \rho \int dr_1\, dr_2\, f^*(r_1) f(r_2)\, D(r_1,r_2) \qquad (7.7.18)$$

Substituting (7.7.13) and (7.7.18) in (7.7.9), we obtain the differential equation for f(r)

$$(\hbar^2/2m)\,\nabla_1^2 f(r_1) + \epsilon \int dr_2\, f(r_2)\, D(r_1,r_2) \qquad (7.7.19)$$

This equation can be solved to give

$$f(r) = Ae^{ik.r} \qquad (7.7.20)$$

where **k** is an arbitrary nonzero and A is constant. Substituting this value of f(r) in (7.7.19), we get

$$-(\hbar^2k^2/2m) + \epsilon \int dr_{12} \exp[ik.r_{12}]\, D(r_{12}) \qquad (7.7.21)$$

which gives an expression for the excitation energy

$$\epsilon(\mathbf{k}) = (\hbar^2k^2/2mS(\mathbf{k})) \qquad (7.7.22)$$

where $S(\mathbf{k})$ is the Fourier transform of $D(r_{12})$

$$S(\mathbf{k}) = \int dr_{12} \exp[i\mathbf{k}.\mathbf{r}_{12}]\, D(r_{12}) \qquad (7.7.23)$$

$S(\mathbf{k})$ is known as the structure factor of the liquid. Equation (7.7.23) is the Feyman formula for the energy of an elementary excitation. We can determine $S(\mathbf{k})$ from neutron scattering. For small **k**, $\epsilon(\mathbf{k})$ increases linearly (phonons). For large k, $S(\mathbf{k})$ has a maximum, which makes a minimum in the $\epsilon(\mathbf{k})$ curve (rotons).

Feyman's formula gives an $\epsilon(\mathbf{k})$ versus **k** curve similar to Landau's as shown in Fig.7.9.

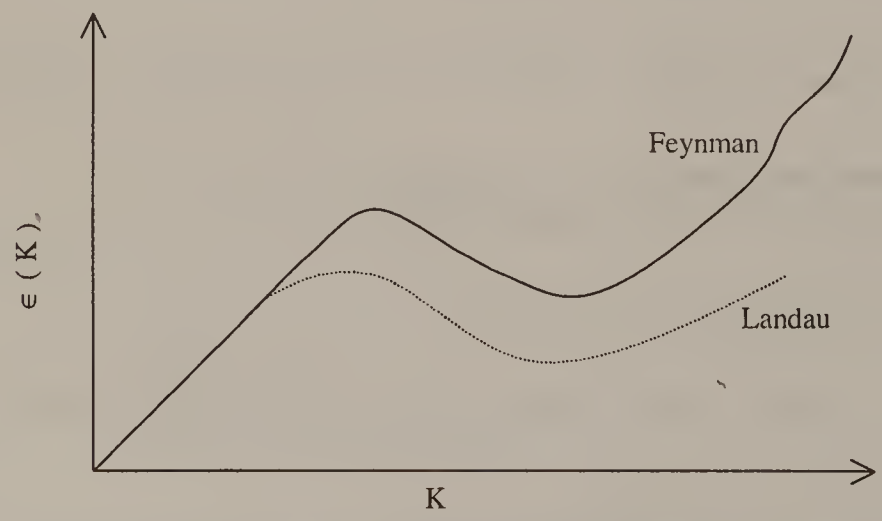


Fig.7.9. Energy spectrum of elementary excitations of liquid HeII in Feynman's theory. Dotted line represents the energy spectrum of Landau theory (reproduced with permission from R.P. Feynman. Progress in Low Temperature Physics, Vol.1, North Holland, Amsterdam).

Near the minimum of roton spectrum, its energy in terms of wave vector k is

$$\epsilon(k) = \Delta + \hbar^2(k - k_0)^2/2\mu \qquad (7.7.24)$$

The theoretical value of the gap Δ is about twice of that found from the Landau curve. However, the minimum of the roton part is at about the right value of k. This discrepancy is expected to be due to the form of the variational wave function used. Later, Feyman, improved the result by constructing a new wave function.

The existence of phonons and rotons has been established experimentally by neutron scattering on liquid He^4. The experimental values of the Landau constants are

$$c = 240 \text{ m/s}$$

$$\Delta/k = (8.65 \pm 0.4) \text{ K}$$

$$k_0 = p_0/\hbar = (1.92 \pm 0.01) \text{ Å}^{-1}$$

$$\mu = (0.16 \pm 0.01) \text{ m}$$

where m is the atomic mass of He^4.

The Landau-Feynman theory has made it plausible that the excitation energy formula (7.6.3) is valid for the very low excited states of liquid HeII.

7.8. Superfluidity

Liquid HeII is a quantum liquid with the energy spectrum represented by

$$\epsilon(P) = cp \qquad \text{(phonons)}$$

$$= \Delta + (p - p_0^2)/2\mu \qquad \text{(rotons)} \qquad (7.8.1)$$

Liquid He^4 below the critical temperature displays superfluidity. The superfluid possesses a remarkable property of flowing through narrow capillary tubes without exhibiting viscosity. At absolute zero, the entire liquid is in its superfluid phase, i.e. in its ground state.

The superfluidity of liquid HeII is a consequence of the properties of energy spectrum.

Let us consider a large volume of liquid at absolute zero through which a solid body is moving. In case of a normal fluid, viscous forces act on the body, and work will be done against them. The work done will be transferred to heat the fluid. Thus the state of lower energy of the fluid will change to that of higher energy. This process will create the elementary excitations in the fluid. Landau shows that such excitations are impossible in liquid HeII due to the shape of the energy spectrum.

Let us assume that the liquid contains no excitations. When the body moves through the liquid, it creates some excitations. Let n(P) be the number of excitations with momentum P and energy $\epsilon(P)$, then the increase in energy of the liquid is

$$\delta E_L = \sum_p n(\mathbf{P})\, \epsilon(\mathbf{P}) \qquad (7.8.2)$$

and the increase in momentum is

$$\delta P_L = \sum_p n(\mathbf{P})\, \mathbf{P} \qquad (7.8.3)$$

On the other hand, if P_i and P_f be the initial and final momenta of the body, the change in energy of the body is

$$\delta E_B = (P_f^2/2M) - (P_i^2/2M) \tag{7.8.4}$$

and the change in momentum is

$$\delta \mathbf{P}_B = \mathbf{P}_f - \mathbf{P}_i \tag{7.8.5}$$

where M is the mass of the body.
Equation (7.8.4) can be written as

$$\delta E_B = (\mathbf{P}_f + \mathbf{P}_i).(\mathbf{P}_f - \mathbf{P}_i) / 2M = (2\mathbf{P}_i + \delta \mathbf{P}_B).\ \delta \mathbf{P}_B / 2M = \mathbf{v}_i.\ \delta \mathbf{P}_B + (\delta \mathbf{P}_B)^2 / 2M \tag{7.8.6}$$

where $\mathbf{v}_i = \mathbf{P}_i / M$ is the initial velocity. From (7.8.2) and (7.8.3), we find that

$$\delta E_L \geq \sum_p n(\mathbf{P})\ |\mathbf{P}|\ |\in(\mathbf{P})/\mathbf{P}|_{min} \geq |\delta \mathbf{P}_L|\ |\in(\mathbf{P})/\mathbf{P}|_{min} \tag{7.8.7}$$

where $|\in(\mathbf{P})/\mathbf{P}|_{min}$ is the minimum value of the ratio $|\in(P)/P|$.

We assume that energy and momentum are conserved in the transition in which the excitations are created in the liquid. Thus

$$\delta E_L = \delta E_B \tag{7.8.8a}$$

$$\delta P_L = \delta P_B \tag{7.8.8b}$$

Substituting (7.8.6) and (7.8.7) in (7.8.8a) and using (7.8.8b), we get

$$\mathbf{v}_i.\ \delta \mathbf{P}_L + (\delta \mathbf{P}_L)^2 / 2M \geq |\delta \mathbf{P}_L|\ |\in(\mathbf{P})/\mathbf{P}|_{min}$$

which gives

$$\mathbf{v}_i + |\delta \mathbf{P}_L/2M| \geq |\in(\mathbf{P})/\mathbf{P}|_{min} \tag{7.8.9a}$$

or

$$(\mathbf{v}_i + \mathbf{v}_f)/2 \geq |\in(\mathbf{P})/\mathbf{P}|_{min} \tag{7.8.9b}$$

When the difference $|v_f - v_i|$ is neglected, we can write

$$\mathbf{v} \geq |\in(\mathbf{P})/\mathbf{P}|_{min} \tag{7.8.10}$$

This inequality condition must be satisfied for the creation of the elementary excitations. Accordingly, if

$$\mathbf{v}_i < |\in(\mathbf{P})/\mathbf{P}|_{min} \tag{7.8.11}$$

no excitation can be created in the liquid and hence, the liquid will be in the superfluid phase. Equation (7.8.11) is known as the Landau criterion for superfluidity. The velocity v_c defined by

$$v_c = |\in(\mathbf{P})/\mathbf{P}|_{min} \tag{7.8.12}$$

is called the critical velocity of superflow. It imposes an "upper limit" on the velocity of the flow up to which the liquid exhibits the superfluid behaviour.

The theoretical value of v_c is of special interest as it is the transition velocity. If the liquid has a particle like spectrum with $\in(P) = P^2/2M$, then $v_c = |\in(\mathbf{P})/\mathbf{P}|_{min}$ will be zero. Such a system cannot be a superfluid. Thus, we find that an ideal Bose gas which does undergo the phenomenon of Bose-Einstein condensation, cannot display superfluidity. However, liquid with energy-spectrum $\in(P)$ for which $v_c > 0$, exhibits the phenomenon of superfluidity.

Let us now consider liquid HeII with the energy spectrum (7.6.3). For phonons, since $\in(P) = cp$, we have

$$v_c = |\in(P)/P|_{min} = C \quad 240 \text{ m/s} \tag{7.8.13}$$

In order to calculate the critical velocity v_c for rotons, we write

$$\in(P)/P = ((p - p_0)^2/2\mu p) + (\Delta/p) \tag{7.8.14}$$

Equation (7.8.14) will be minimum, if

$$(\partial/\partial p)|\in(P)/P| = 0$$

or

$$p^2 = p_0^2 + 2\mu\Delta \tag{7.8.15}$$

Substituting this value in (7.8.14), we get

$$v_c = |\in(\mathbf{P})/\mathbf{P}|_{min} = [(p_0^2 + 2\mu\Delta)^{1/2} - p_0]/\mu \quad \Delta/p_0 \quad 63 \text{ m/s} \tag{7.8.16}$$

Thus we conclude that the liquid HeII exhibits superfluidity if the velocity of the flow is less than about 63 m/s. However, the theoretical value of v_c is large in comparision with the experimental value. In this case, no phonons or rotons can be created. At nonzero temperature where there already exist some phonons and rotons, new phonons and rotons cannot be created owing to the motion of liquid helium. At nonzero temperature, when the walls of the vessel are in motion, a part of the mass of the liquid helium will behave as a normal fluid, and the other part will behave as a superfluid having no viscosity. There is no friction between these two parts of the liquid moving through each other. Thus, we may regard the liquid helium as a mixture of two fluids – superfluid and normal fluid.

7.9. Quantized Vortices

In this section, we discuss the theory of quantized vortices, which is related to the theory of the superfluid velocity v_S. A common type of (classical) vortex consists of a central 'core' of radius a in which the fluid rotates as a solid body with angular velocity, say, ω. Onsager and Feyman showed that a possible wave function of the superfluid would lead to a circulation motion analogous to classical vortex motion, which established the physical basis for the existence of a quantized vortex motion in the fluid.

We consider the wave function which represents the state of liquid HeII at absolute zero flowing with a uniform mass velocity. The system is in the ground state with superfluid component only, so there is no excitation. Let $\Psi_0(r_1, r_2, ..., r_N)$ be the ground state wave function when the superfluid is at rest. Then the wave function of the superfluid moving with a uniform translational velocity v_S is given by

$$\Psi = \Psi_0 \exp [i\mathbf{K}. \sum_i \mathbf{r}_i] \tag{7.9.1}$$

where r_i is the position vector of atom i of the system and the wave vector **K** is

$$\mathbf{K} = p/\hbar = mv_S/\hbar$$

We now consider a chain of atoms constituting a ring (Fig.7.10).

Let each atom be displaced from its original position in the ring to a position of its nearest neighbour. The net result is that we obtain a configuration which is physically identical to the original configuration. Because of the symmetrical properties of the boson wave function, this operation will not change the wave function. The change in phase of the wave function is given by

$$\Delta\phi = (m/\hbar) \Sigma \mathbf{v}_s. \Delta\mathbf{r}_i \approx (m/\hbar) \oint \mathbf{v}_s.d\mathbf{l} \tag{7.9.2}$$

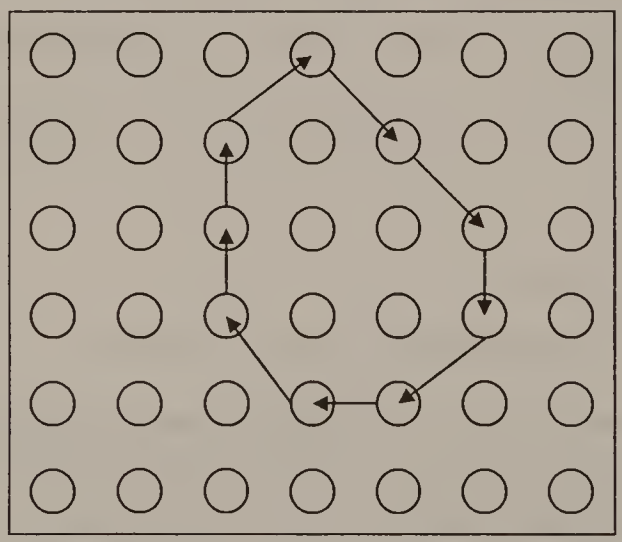


Fig.7.10. A chain of atoms constituting a ring. If all the atoms are displaced around the ring, the wave function is unchanged.

In view of the symmetry nature of the wave functions, the phase change $\Delta\phi$ must be an integral multiple of 2π. Thus

$$(m/\hbar) \oint_c \mathbf{v}_s.d\mathbf{l} = 2\pi n$$

or

$$\Gamma_c = \oint_c \mathbf{v}_s.d\mathbf{l} = 2\pi n(\hbar/m) \tag{7.9.3}$$

where Γ_c is the circulation of fluid round any curve c and n is an integer. Thus we arrive at the important conclusion that the circulation of the superfluid velocity field is quantised, and the quantum of vorticity is $2\pi\hbar/m$.

If we apply Stokes' theorem to such a vortex model, we obtain the result

$$\int_S (\nabla \times v_s).dS = 2\pi n\hbar/m \qquad (7.9.4)$$

where S denotes the area enclosed by the circle of integration. This is a general result. If we shrink the core to infinitesimal dimensions in such a way that the strength of the vortex ($\hbar$/m) remains constant, we get what is called a vortex line. We can assume vortex lines with different quantized values of the circulation corresponding to n= 1, 2, 3, ... When the velocity v_s is continuous throughout the area, then for a simply-connected area of fluid, the circulation Γ_c shrinks continuously, and finally tends to zero because the integral of (7.9.4) decreases continuously. However, in such a case the quantum number n must be zero. This implies that in a simply-connected region for which the velocity field is continuous, we have the condition

$$\nabla \times \mathbf{v}_s = 0 \qquad (7.9.5)$$

which has been postulated by Landau for the velocity of superfluid flow. Thus, the motion of the fluid is irrotational. The Landau condittion in a simply connected region requires that $v_s = 0$. On the other hand, in the normal fluid,

$$\nabla \times \mathbf{v} = 2\omega$$

and the free surface of the rotating fluid is parabolic in shape. It seems that the motion of the superfluid is quite different from that of the normal fluid. It is quite contrary to experiment. The superfluid component of liquid HeII appears to rotate practically in the same manner as the normal component.

Thus, two mutually contradicting ideas are appearing in the superfluid component of liquid HeII. On one hand, the superfluid is flowing with velocity $\mathbf{v}_s$ and on the other, $\nabla \times \mathbf{v}_s$ does not vanish.

In a multiple-connected region, it is found that $\Gamma_c \neq 0$ even if $\nabla \times \mathbf{v} = 0$ everywhere. This suggests that one can achieve non-zero circulations in a simply-connected region containing the superfluid if there are singular regions in the fluid which make it multiply connected. For example, when we consider a classical vortex line, it consists of a central core of radius a in which liquid rotate as a solid body with angular velocity ω and hence the circulation around the classical vortex line is nonzero. Outside the core, the velocity field is inversely proportional to r, the distance from the line, and is irrotational everywhere. We consider the elemental area between circles of radii r and r + dr (Fig.7.11). Let n(r) be the number density of the vortex lines, each of constant circulation of $\hbar$/m, in the fluid. Then, the sum of the circulations of the individual vortices is

$$2\pi r\, dr\, n(r)\, \hbar/m \qquad (7.9.6)$$

The net circulation around the boundaries is given by

$$2\pi\,(r+dr)\,(v+(dv/dr)dr) - 2\pi rv \quad 2\pi\,(d/dr)(rv)\,dr \qquad (7.9.7)$$

where v(r) is the velocity field at a distance r from the axis of rotation. Since the net circulation around the boundary is equal to the sum of the circulations of the vortices, we have

$$2\pi\,(d/dr)(rv)\,dr = 2\pi r\, dr\, n(r)\, \hbar/m$$

or

$$(d/dr)(rv) = r\, n(r)\, \hbar/m \qquad (7.9.8)$$

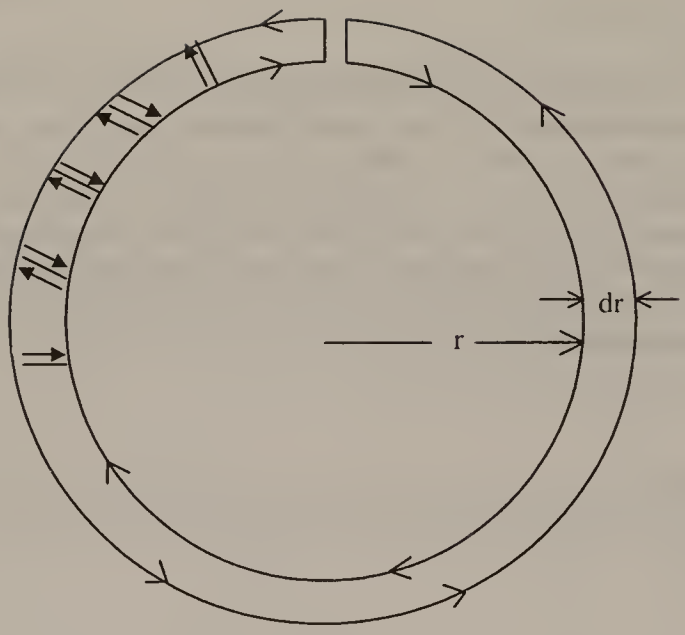


Fig.7.11. A model for rotation of the superfluid for calculating the velocity field.

Let us consider some special cases. If we have a uniform array of vortex lines, n(r) is a constant, say C, and (7.9.8) gives the velocity field.

$$v(r) = \omega r \tag{7.9.9}$$

where $\omega = C\hbar/2m$ is the angular velocity. On the other hand, in the absence of the vortex line density, n(r) = 0, and we get from (7.9.8) the velocity field

$$v(r) = A/r \tag{7.9.10}$$

where A is constant, which is irrotational and satisfied the Landau condition everywhere except at the axis (r=0). If we apply Stokes' theorem to such a vortex model, we obtain the result for circulation

$$\Gamma_c = \int_0^{2\pi} vr\, d\theta = \int_0^{2\pi} (A/r)\, r\, d\theta = 2\pi A \tag{7.9.11}$$

This agrees with the general result (7.9.3) if $A = \hbar/m$. Thus the velocity at the radius r is $\hbar/mr$.

We now consider the enrgy associated with this state of fluid. The energy of the vortex line per unit length is given by

$$E = \int_a^R (1/2)\, [2\rho\pi r\, dr]\, v^2(r) = (\pi\rho\hbar^2/m^2) \int_a^R (dr/r) = (\pi\rho\hbar^2/m^2) \ln (R/a) \tag{7.9.12}$$

where ρ is the mass density of the fluid, R is the radius of the cylindrical vessel containing the line, and a, the radius of the core of a vortex line. Value of a is uncertain. Feyman suggests that a $\sim 10^{-10}$m. Thus,

in most of the region of the superfluid, the velocity field is irrotational i.e. $\nabla \times \mathbf{v}_s = 0$. It is only very narrow regions of the fluid, where the motion is rotational. Thus, we have obtained a suitable model for the superfluid, where two elements namely, solid-body rotation and curl-free circulation, which seem to be diametrically opposite, are made consistent.

Finally, we discuss the nature of quantum vortices. The vortex line cannot terminate within the body of the liquid- it may terminate either on the walls of the container or on the free surface of the liquid. In general, a vortex line may be curved, and it may not terminate on the boundries, or on the free surface. In that case, a vortex may be a continuous curve like the smoke ring, known as a vortex ring. The fundamental quantisation condition (7.9.11) is also valid for a vortex ring.

Problems

7.1 There are g cells of energy ϵ. Show that the number n of bosons of energy ϵ distributed among these cells is given by
$n = g / (e^{(\epsilon - \mu)/kT} - 1)$
What is μ and how will you find it.

7.2 Show that the equation of state of an ideal Bose gas in the gaseous phase is given by
$PV/NkT = 1 - (1/2^{5/2})(\rho\lambda^3)((1/8) - (2/3^{3/2}))(\rho\lambda^3)^2 - \ldots$

7.3 Discuss the phenomenon of Bose-Einstein condensation. How does it differ from ordinary vapour condensation. Calculate the critical temperature at which condensation into the lowest order starts.

7.4 Obtain an expression for the specific heat of a Bose gas. Discuss its variation with temperature.

7.5 A gas of N bosons of mass m is contained in a vessel V. Calculate the critical temperature at which condensation begins.

7.6 Discuss an ideal gas obeying Bose-Einstein statistics in a two-dimensional space. Does Bose-Einstein condensation occur in this case ?

7.7 Derive an expression for the energy distribution of bosons and discuss its application for the interpretation of the anomalous properties of liquid He^4.

7.8 Discuss how far the Bose-Einstein distribution law explains the properties of liquid He^4.
Is this distribution law also applicable to liquid He^3 ?

7.9 Derive Planck's formula for black-body radiation using Bose-Einstein statistics. Using this result, deduce the Stefan-Boltzman law.

7.10 Show that the specific heat per unit volume of the photon gas is given by
$C_v = (4\pi^2 k^4 / 15 C^3 \hbar^3) T^3$

7.11 Derive the Planck radiation formula for a two-dimensional space and hence deduce the Stefan-Boltzmann law.

CHAPTER 8

IDEAL FERMI SYSTEM

Particles having a half-odd integral spin (in units of $\hbar$) are called fermions. Unlike bosons, in addition to the indistinguishability, they obey the Pauli exclusion principle. This imposes special restriction on the distribution of fermions among the possible states. The fermions, which obey the Fermi-Dirac (FD) statistics, include

(i) electrons
(ii) positrons
(iii) nucleons (protons and neutrons) and
(iv) He^3

Electrons are of the greatest interest and considered mainly in this chapter.

8.1. Ideal Fermi Gas: Weakly Degenerate

We consider an ideal Fermi gas, which obeys Fermi-Dirac statistics. For such a gas, the total number of particles and the total energy are given by

$$N = \sum_i n_i = \int_0^\infty g(\epsilon)\, d\epsilon \,/(z^{-1}e^{\beta\epsilon}+1) \tag{8.1.1}$$

$$U = \sum_i \epsilon_i n_i = \int_0^\infty \epsilon\, g(\epsilon) d\epsilon \,/(z^{-1}e^{\beta\epsilon}+1) \tag{8.1.2}$$

where $\beta=(kT)^{-1}$ and $z = e^{\beta\mu}$. In this case, the particles will be distributed among the various quantum states, so that no more than one particle can be in each quantum state (Pauli exclusion principle).

As derived in Sec.7.1, the number of quantum states with energy ϵ and $\epsilon+d\epsilon$ is given by

$$g(\epsilon)d\epsilon = (2\pi gV/h^3)\,(2m)^{3/2}\,\epsilon^{1/2}\,d\epsilon \tag{8.1.3}$$

Using this value of $g(\epsilon)d\epsilon$ in Eqs. (8.1.1) and (8.1.2), we get

$$N = (2\pi gV/h^3)\,(2m)^{3/2}\,F_{3/2}\,(z) \tag{8.1.4}$$

$$U = (2\pi gV/h^3)\,(2m)^{3/2}\,F_{5/2}\,(z) \tag{8.1.5}$$

where

$$F_n(z) = \int_0^\infty \epsilon^{(n-1)} d\epsilon \,/\, (z^{-1}e^{\beta\epsilon} + 1) \tag{8.1.6}$$

Putting $\beta\epsilon = x$, the function $F_n(z)$ can be written in the form

$$F_n(z) = (kT)^n \int_0^\infty (x^{n-1} / (z^{-1}e^x + 1))\, dx = (kT)^n)\, \Gamma(n)\, f_n(z) \tag{8.1.7}$$

where

$$f_n(z) = (1/\Gamma(n)) \int_0^\infty (x^{n-1} / (z^{-1}e^x + 1))\, dx \tag{8.1.8}$$

and $\Gamma(n)$ is the Gamma function. Then, we get

$$N = (gV/\lambda^3)\, f_{3/2}(z) \tag{8.1.9}$$

$$U = (3/2)\, kT\, (gV/\lambda^3)\, f_{5/2}(z) \tag{8.1.10}$$

where

$$\lambda = (h^2/2mkT)^{1/2} \tag{8.1.11}$$

is the thermal wavelength.
When z is small, $(z^{-1}e^x + 1)^{-1}$ can be expanded in the form

$$1/(z^{-1}e^x + 1) = z\, e^{-x}(1 + ze)^{-1} = \sum_{l=1}^\infty (-1)^{l-1}\, z^l\, e^{-lx}$$

and hence $f_n(z)$ can be evaluated as

$$f_n(z) = (1/\Gamma(n)) \sum_{l=1}^\infty (-1)^{l-1}\, z^l \int_0^\infty e^{-lx}\, x^{n-1}\, dx$$

$$= \sum_{l=1}^\infty (-1)^{l-1}\, (z^l / l^n)$$

$$= z - (z^2/2^n) + (z^3/3^n) - (z^4/4^n) + \ldots \tag{8.1.12}$$

In order to determine the thermodynamic properties of the Fermi gas, we must know the fugacity z as a function of the particle density $\rho(=N/V)$ and temperature T. From Eq.(8.1.9)

$$f_{3/2}(z) = (\rho\lambda^3/g) = (\rho/g)\, (h^2/2\pi mkT)^{3/2} \tag{8.1.13}$$

Now in the case of very low density and high temperature, where

$$f_{3/2}(z) = (\rho/g)\, (h^2/2\pi mkT)^{3/2} \ll 1 \tag{8.1.14}$$

the gas is said to be highly nondegenerate. From (8.1.12), this condition implies that $z \ll 1$ and hence

$$f_n(z) = z$$

Then, Eqs.(8.1.9) and (8.1.10) reduce to

$$N = gVz / \lambda^3 \tag{8.1.15}$$

$$U = (3/2)\, kT\, (gVz/\lambda^3) = (3/2)NkT \tag{8.1.16}$$

Equation (8.1.16) is the standard result for an ideal classical gas.

If z is small in comparison to unity but not very small, we use Eq.(8.1.12). From (8.1.9) and (8.1.10), we get

$$U = (3/2)\, NkT\, (f_{5/2}(z)/f_{3/2}(z)) \tag{8.1.17}$$

Now it can be shown that

$$\begin{aligned} f_{5/2}(z)/f_{3/2}(z) &= 1 + (1/2^{5/2})\, f_{3/2}(z) - ((2/3^{5/2}) - (1/2^3))\, (f_{3/2}(z))^2 + \ldots \\ &= 1 + (1/2^{5/2})\, (N\lambda^3/Vg) - ((2/3^{5/2}) - (1/2^3))(N\lambda^3/Vg)^2 + \ldots \end{aligned} \tag{8.1.18}$$

Then

$$U = (3/2)\, NkT\, [1 + (1/2^{5/2})(N\lambda^3/Vg) - ((2/3^{5/2}) - (1/2^3))(N\lambda^3/Vg)^2 + \ldots] \tag{8.1.19}$$

and the specific heat is

$$C_v = (3/2)Nk\, [1 - (1/2^{7/2})(N\lambda^3/Vg) + ((2/3^{5/2}) - (1/2^3))(N\lambda^3/Vg)^2 + \ldots] \tag{8.1.20}$$

The first term of Eqs. (8.1.19) and (8.1.20) are, respectively, the energy and specific heat in the Boltzmann limit and the second and third terms give the first and second order correction due to the deviation from the classical behaviour.

Using the relation

$$PV = (2/3)\, U \tag{8.1.21}$$

one can obtain the equation of state in the form of the virial expansion:

$$PV = NkT\, [1 + (1/2^{5/2})(\rho\lambda^3/g) - ((2/3^{5/2}) - (1/2^3))\, (\rho\lambda^3/g)^2 + \ldots] \tag{8.1.22}$$

The correction terms depend on the value of the quantity $(\rho\lambda^3/g)$. The correction term will be small, when

$$(N/Vg)\, (h^2/2\pi mkT)^{3/2} \ll 1$$

For this, the gas should be sufficiently rarefied or the temperature T should be high. At very high temperatures, the correction terms will be very small and may be neglected, leading to the classical properties. Thus we see that the deviation from the classical behaviour occurs when the temperature is

lowered at constant density. The deviations in this case cause an increase in pressure and energy but a decrease in specific heat.

When the temperature and density are such that $((\rho\lambda^3/g)$ is of the order of unity, the gas is said to become degenerate, and this expansion formalism cannot be of much use.

8.2. Ideal Fermi Gas: Strongly Degenerate

At sufficiently low temperature, $(\rho\lambda^3/g) \gg 1$ and the gas becomes degenerate. When $(\rho\lambda^3/g) \to \infty$, which corresponds to $T = 0$, the gas is completely degenerate.

Let us consider a Fermi gas in a degenerate state $(N\lambda^3/Vg \gg 1)$. The mean occupation number of the single particle state ϵ is

$$<n_\epsilon> = 1/(e^{(\epsilon-\mu)/kT} + 1) \tag{8.2.1}$$

where μ is the chemical potential, which is a function of T, i.e. $\mu = \mu(T)$. The number of quantum state with the translational motion of a particle in the energy range ϵ and $\epsilon+d\epsilon$ is given by (8.1.3), i.e.

$$g(\epsilon)d\epsilon = (2\pi gV/h^3)\,(2m)^{3/2}\,\epsilon^{1/2}\,d\epsilon \tag{8.2.2}$$

Combining Eqs.(8.2.1) and (8.2.2), the number of particles in the energy range ϵ and $\epsilon+d\epsilon$ is given by

$$\begin{aligned} n(\epsilon)d\epsilon &= g(\epsilon)d\epsilon/(e^{(\epsilon-\mu)/kT} + 1) \\ &= (2\pi gV/h^3)\,(2m)^{3/2}\,(\epsilon^{1/2}d\epsilon/(e^{(\epsilon-\mu)/kT} + 1)) \end{aligned} \tag{8.2.3}$$

The total number of particles in the gas is obtained by integrating Eq.(8.2.3) in the limit $\epsilon = 0$ and $\epsilon=\infty$:

$$N = (2\pi gV/h^3)\,(2m)^{3/2} \int_0^\infty \epsilon^{1/2}d\epsilon/(e^{(\epsilon-\mu)/kT} + 1) \tag{8.2.4}$$

The total energy of the gas is

$$U = (2\pi gV/h^3)\,(2m)^{3/2} \int_0^\infty \epsilon^{3/2}d\epsilon/(e^{(\epsilon-\mu)/kT} + 1) \tag{8.2.5}$$

For simplicity, we first consider a Fermi gas in a state of complete degeneracy. In the limit $T \to 0$, where $\mu \to \mu(0) \equiv \mu_0$, the mean occupation number becomes

$$\begin{aligned} <n_\epsilon> &= 1 \qquad \text{for } \epsilon < \mu_0 \\ &= 0 \qquad \text{for } \epsilon > \mu_0 \end{aligned} \tag{8.2.6}$$

The limiting chemical potential μ_0 is called the Fermi energy ϵ_F of the system. The variation of $<n_\epsilon>$ at absolute zero temperature is shown by a continuous curve in Fig.8.1. Thus at $T = 0$, all single particle states up to $\epsilon = \epsilon_F$ are completely filled with one particle in each state according to Pauli's exclusion principle. On the other hand, all single particle states with $\epsilon > \epsilon_F$ are empty. Thus, the Fermi

energy ϵ_F has a physical meaning. It is the energy of the top most occupied level at T = 0. Such a behaviour cannot be shown in case of Bose gas.

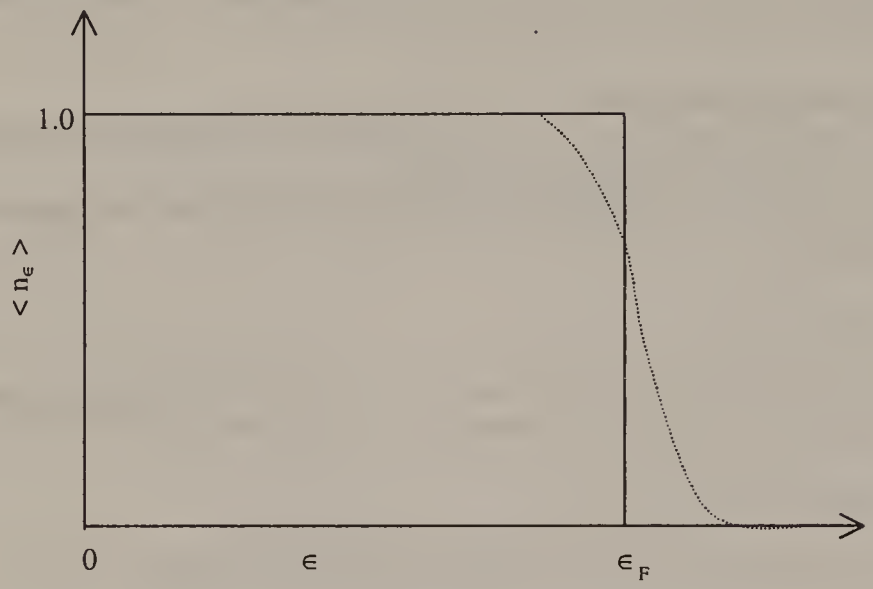


Fig.8.1. Fermi-Dirac mean occupation number $<n_\epsilon>$ as a function of ϵ :(a) at T = 0 represented by solid line and (b) at T>0 represented by dashed line.

The energy distribution of the Fermi gas is given (8.2.3). Figure 8.2 shows this distribution at T = 0. The sharp cut-off at $\epsilon = \epsilon_F$ shows the behaviour of $<n_\epsilon>$.

Using Eq.(8.2.6) at T = 0, Eq.(8.2.4) reduces to

$$N = (2\pi gV/h^3)(2m)^{3/2} \int_0^{\epsilon_F} \epsilon^{1/2} d\epsilon$$

$$= (4\pi gV/3h^3)(2m)^{3/2} \epsilon_F^{3/2} \qquad (8.2.7)$$

so that the Fermi energy ϵ_F is

$$\epsilon_F = (3N/4\pi gV)^{2/3} (h^2/2m) = (3\rho/4\pi g)^{2/3} (h^2/2m) \qquad (8.2.8)$$

where $\rho = N/V$ is the particle density. Thus the Fermi energy ϵ_F depends on the particle density ρ and on the mass m of the particle. The Fermi temperature T_F is defined by

$$\epsilon_F = kT_F \qquad (8.2.9)$$

Substituting Eq.(8.2.6) in Eq.(8.2.5) the total ground state energy of the gas is given by

$$U_0 = (2\pi gV/h^3)(2m)^{3/2} \int_0^{\epsilon_F} \epsilon^{3/2} d\epsilon = (4\pi gV/5h^3)(2m)^{3/2} \epsilon_F^{5/2} \qquad (8.2.10)$$

From (8.2.7) and (8.2.10), we get

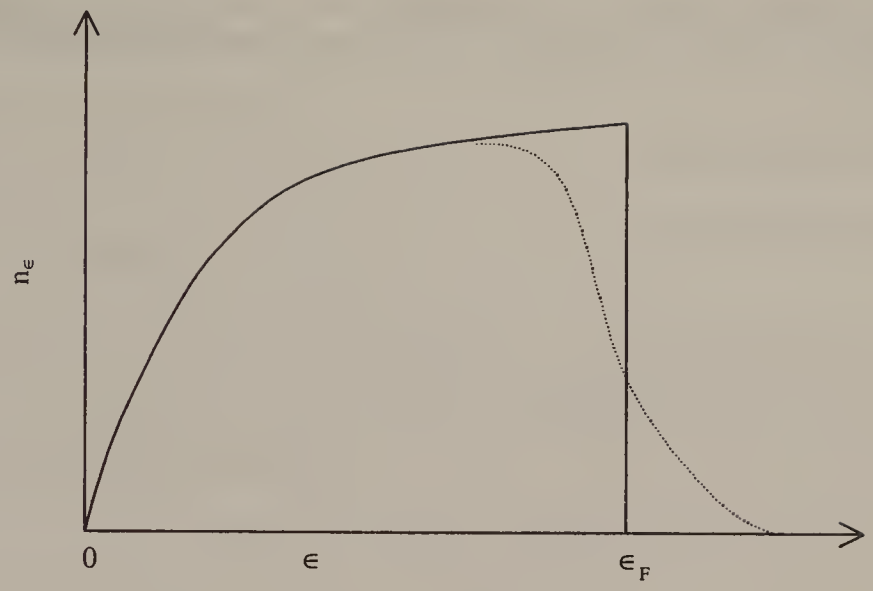


Fig.8.2. Variation of Fermi-Dirac energy distribution (a) at T = 0 represented by solid line and (b) at T > 0 represented by dashed line.

$$U_0/N = (3/5)\,\epsilon_F \tag{8.2.11}$$

Thus, the average energy per particle of the Fermi gas at T = 0 is 3/5 times the Fermi energy ϵ_F.

Finally the ground state equation of state of the gas at T = 0 is

$$P_0 = (2/3)\,(U_0/V) = (2/5)\,(N\epsilon_F/V) = (2/5)\,\rho\epsilon_F \tag{8.2.12}$$

or substituting the value of ϵ_F

$$P_0 = (2/5)\,(3/4\pi g)^{2/3}\,(h^2/2m)\,\rho^{5/3} \tag{8.2.13}$$

i.e.

$$P_0 \propto \rho^{5/3} \tag{8.2.14}$$

Thus the pressure of a Fermi gas at T = 0 is proportional to the (5/3) power of the density.

So far we have considered a Fermi gas at zero temperature. Now we consider it at finite temperature. At $T \ll T_F$, the mean occupation number $\langle n_\epsilon \rangle$ and energy distribution $n(\epsilon)$ are very similar to those at T = 0, shown in Fig.8.1 and 8.2. Such a gas is called extremely degenerate. The mean occupation number $\langle n_\epsilon \rangle$ and energy distribution $T < T_F$ are shown by dashed lines in Figs 8.1 and 8.2. The solid lines correspond to curves for T = 0. As the temperature T is raised from T = 0, the particles are excited from single particle states with energy $\epsilon < \epsilon_F$ to single particle states with energy $\epsilon > \epsilon_F$. This transition is only in a narrow range of the value of the energy ϵ, close to the Fermi energy ϵ_F. The width of this transition zone of the Fermi distribution is of the order of kT. The major part of the system remains unaffected by the rise in temperature; only a fraction of the particles is in the thermally excited states.

For a study of a Fermi gas at finite but low temperature, where z >1, we take (8.2.4) and (8.2.5) for the total number of particles and total energy of the system, which can be expressed as [see Eqs.(8.1.4) and (8.1.5)]

$$N = (2\pi gV/h^3)(2m)^{3/2} F_{3/2}(z) \tag{8.2.15}$$

$$U = (2\pi gV/h^3)(2m)^{3/2} F_{5/2}(z) \tag{8.2.16}$$

where

$$F_n(z) = \int_0^\infty \epsilon^{(n-1)} d\epsilon \,/\, (e^{(\epsilon-\mu)/kT} + 1) \tag{8.2.17}$$

In order to solve the integral of (8.2.17) when z is large (z>1), we put $(\epsilon-\mu)/kT = x$, then

$$F_n(z) = kT \int_{-\mu/kT}^{\infty} ((\mu + kTx)^{n-1}/(e^x+1))dx$$

$$= kT \int_0^{\mu/kT} ((\mu - kTx)^{n-1}/(e^{-x}+1))dx + kT \int_0^{\infty} ((\mu - kTx)^{n-1}/(e^x+1))dx$$

Using the relation

$$1/(e^{-x}+1) = 1 - (1/(e^x+1))$$

$F_n(z)$ can be written as

$$F_n(z) = \int_0^{\mu} \epsilon^{n-1} d\epsilon - kT \int_0^{\mu/kT} ((\mu - kTx)^{n-1}/(e^x+1))dx + kT \int_0^{\infty} ((\mu - kTx)^{n-1}/(e^x+1))dx$$

$$= (\mu^n/n) + kT \int_0^{\infty} \{((\mu + kTx)^{n-1} - (\mu - kTx)^{n-1})/(e^x+1)\}dx + kT \int_{\mu/kT}^{\infty} ((\mu - kTx)^{n-1}/(e^x+1))dx$$

Since $\mu/kT \gg 1$, the contribution of the last integral is very small and can be neglected. Thus after expanding

$$(\mu \pm kTx)^{n-1} = \mu^{n-1}(1 \pm kTx/\mu)^{n-1}$$

we obtain

$$F_n(z) = \mu^n[(1/n) + 2(n-1)(kT/\mu)^2 f_2(1) + ((n-1)(n-2)(n-3)/3)(kT/\mu)^4 f_4(1) + \ldots]$$

where the function $f_m(1)$ is defined from (8.1.8). Thus,

$$f_m(1) = \sum_{l=1}^{\infty} (-1)^{l-1} (1/l^m) = (1 - 2^{1-m})\,\xi(m).$$

Here

$$\xi(m) = \sum_{l=1}^{\infty} (1/l^m)$$

is the Riemann zeta function. Then

$$f_m(1) = \pi^2/12 \qquad \text{for } m = 2$$

$$= 7\pi^4/120 \qquad \text{for } m = 4$$

Thus for large z(i.e. $z > 1$), $F_n(z)$ can be evaluated as

$$F_n(z) = (1/n)\mu^n[1 + (\pi^2/6)n(n-1)(kT/\mu)^2 + (7\pi^4/360)n(n-1)(n-2)(n-3)(kT/\mu)^4 + \ldots] \quad (8.2.18)$$

Comparing (8.2.7) and (8.2.15), we get

$$\mu = \epsilon_F [1 + (\pi^2/8)(kT/\mu)^2 + (7\pi^4/640)(kT/\mu)^4 + \ldots]^{-2/3}$$

$$= \epsilon_F [1 - (\pi^2/12)(kT/\mu)^2 + (\pi^4/720)(kT/\mu)^4 + \ldots] \quad (8.2.19)$$

This can be solved by the method of iteration. Thus,

$$\mu \quad \epsilon_F[1 - (\pi^2/12)(T/T_F)^2 - (\pi^4/80)(T/T_F)^4 + \ldots] \quad (8.2.20)$$

The variation of the chemical potential μ of an ideal fermi gas with the absolute temperature T is shown in Fig.8.3. At $T = 0$, the chemical potential is equal to the Fermi energy ϵ_F.

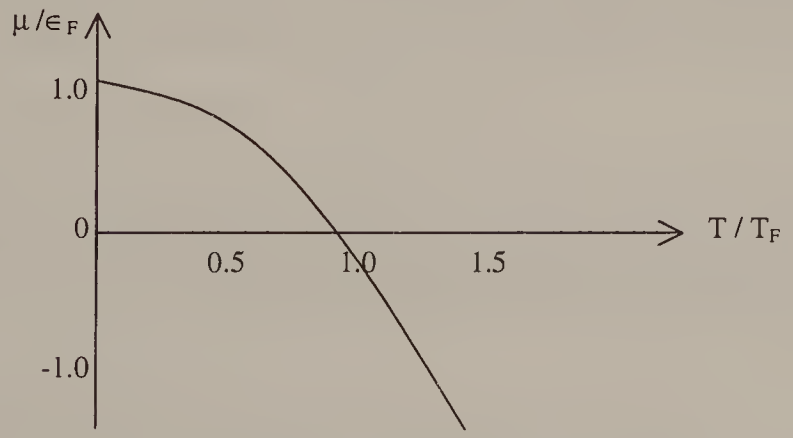


Fig.8.3. Variation of the chemical potential μ of an ideal Fermi gas as a function of T/T_F.

As the temperature increases, the chemical potential decreases and becomes zero at a temperature, just below the Fermi temperature T_F. As the temperature increases further, the chemical potential becomes more and more negative.

Then with the help of Eqs.(8.2.7) and (8.2.20), Eq.(8.2.16) can be written as

$$U = (3/5)N\epsilon_F [1 + (5\pi^2/12)(T/T_F)^2 - (\pi^4/16)(T/T_F)^4 + \ldots] \quad (8.2.21)$$

The variation of energy U with T is shown in Fig.8.4. For ideal Boltzmann gas, U = (3/2)NkT, which is also demonstrated in the figure. It is evident from the figure that the energy of an ideal Fermi gas is always greater than that of an ideal Boltzmann gas.

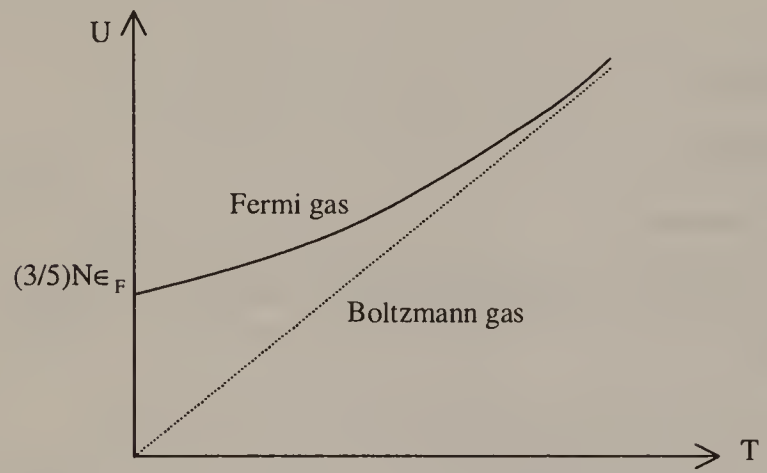


Fig.8.4. Variation of the energy U of an ideal Fermi gas as a function of absolute temperature T.

Then, specific heat of the gas becomes

$$C_v = (\partial U/\partial T)_v = Nk\,[(\pi^2/2)(T/T_F) - (3\pi^4/20)(T/T_F)^3 + \ldots] \qquad (8.2.22)$$

Thus for $T < T_F$, the specific heat of the degenerate Fermi gas varies as

$$C_v = aT + bT^3 \qquad (8.2.23)$$

when $T \ll T_F$

$$C_v = aT \qquad (8.2.24)$$

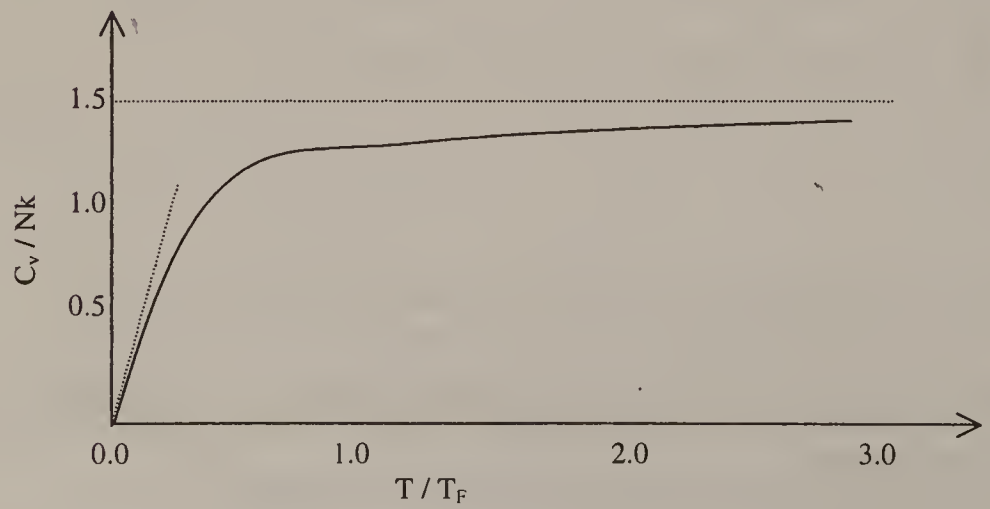


Fig.8.5. Variation of specific heat at constant volume C_v of an ideal fermi gas with absolute temperature T.

Thus, as $T \to 0$, $C_v \to 0$. The variation of C_v with T is shown in Fig.8.5. It is considerably smaller than the classical value (3/2) Nk.
The pressure of the gas is then given by

$$P = (2/3)(U/V) = (2/5)(N\epsilon_F/V)[1+(5\pi^2/12)(T/T_F)^2 - (\pi^4/16)(T/T_F)^4 + \ldots] \quad (8.2.25)$$

The first tem of (8.2.21) and (8.2.25) are the ground state values and other terms are corrections arising due to the rise of temperature.

From (8.2.20) and (8.2.25), the Helmholtz free energy of the degenerate Fermi gas is

$$A = \mu N - PV = N\epsilon_F[1-(5\pi^2/12)(T/T_F)^2 + (\pi^2/48)(T/T_F)^4 + \ldots] \quad (8.2.26)$$

and hence entropy of system is

$$S = Nk[(\pi^2/2)(T/T_F) - (\pi^2/20)(T/T_F)^3 + \ldots] \quad (8.2.27)$$

From this, it is clear that $S \to 0$ when $T \to 0$ in accordance with the third law of thermodynamics.

From the study of degenerate Fermi gas, we conclude that C_v and S vanish at absolute zero whereas U and P remain finite.

8.3. Free Electron Theory of Metals

In metals, the electrons in the outermost shells of the atoms are weakly bound. These electrons become detached, and move freely through the volume of the metal. They are conductors of electricity and many properties of the metals are determined by the motion of these conduction electrons. This is the free electron model. In a solid metal, the positive ions are confined to the near vicinity of their lattice points, whereas the free electrons move freely through the volume of the metal.

Since the electrons have spin half, we treat these electrons as an ideal Fermi gas obeying the Fermi-Dirac statistics. Then the Fermi energy ϵ_F of the electron gas (with g = 2) is [See Eq.(8.2.8)]

$$\epsilon_F = (3\pi^2 N/V)^{2/3}(\hbar^2/2m) = (3\pi^2\rho)^{2/3}(\hbar^2/2m) \quad (8.3.1)$$

In most metals the density is high, and the Fermi temperature T_F is of the order of 10^4-10^5 K, which is larger than a room temperature T = 300° K. This shows that the free electron gas in metals is highly degenerate. Thus we can treat the free electron gas as a degenerate ideal Fermi gas. The theory discussed in the section for the degenerate ideal Fermi gas can be applied to the free electrons in a metal.

Table 8.1. Properties of the Electron gas at the Fermi Surface

	Electron density $\rho(m^{-3})$	Momentum $K_F(m^{-1})$	Energy ϵ_F(ev)	T_F(K)
Li	4.60×10^{25}	1.10×10^9	4.7	5.5×10^4
Na	2.50	0.90	3.1	3.7
K	1.34	0.73	2.1	2.4
Cu	8.50	1.35	7.0	8.2
Ag	5.76	1.19	5.5	6.4
Au	5.90	1.20	5.5	6.4

Let us now discuss the results of the free electron gas. ϵ_F in this case is high because the density ρ is high and the mass of the electron m is very small.

We first consider the case when $T \to 0$, where the total energy of the system is

$$U_0 = (3/5)\, N\epsilon_F = (3N\hbar^2/10m)\,(3\pi^2 N/V)^{2/3} \tag{8.3.2}$$

Then, the equation of state of the electron gas at $T = 0$ is

$$P_0 = (2/5)(N\epsilon_F/V) \tag{8.3.3}$$

This pressure is usually much higher than that of the usual gas, and tends to expand the metal, which is counter balanced by the attractive forces between the atoms within the metal. Thus the free electrons are generally prevented from leaving the metal under this high pressure. However, at very high temperature, some of the electrons may have sufficient energies to escape from the metal.

When the temperature T is raised from T = 0, only a very small portion of the electrons is influenced by temperature, the major part of the system remains unaffected. Accordingly, the chemical potential of the free electron gas is given by [see Eq.(8.2.20)]

$$\mu = \epsilon_F [1 - (\pi^2/12)\,(T/T_F)^2 + \ldots] \tag{8.3.4}$$

At room temperature $T \ll T_F$, μ is only fractionally below the Fermi energy ϵ_F. As a good approximation, the chemical potential at $T \ll T_F$ is equal to the Fermi energy ϵ_F.

In the low temperature limit when $T \ll T_F$ the energy of the free electron gas is given by

$$U = (3/5)\, N\epsilon_F [1 + (5\pi^2/12)(T/T_F)^2 + \ldots] \tag{8.3.5}$$

and the specific heat at constant volume is

$$C_V = (\pi^2/2)\, Nk\,(T/T_F) + 0\,(T/T_F)^3 \tag{8.3.6}$$

From Eq.(8.3.5), it is clear that when $T \ll T_F$, the specific heat of the free electron gas in metal is proportional to the absolute temperature T, i.e.

$$C_V \propto T$$

This vanishes at absolute zero of temperature.

When we consider the specific heat of metal, it is the sum of the contributions of the free electrons and the lattice vibration. Thus,

$$C_V = (C_V)_{\text{electron}} + (C_V)_{\text{lattice}} \tag{8.3.7}$$

where the first term of (8.3.7) is the contribution of the free electrons to the specific heat of a metal and given (8.3.6), and the second term is the contribution of the lattice vibrations. According to the Debye theory, the contribution of the lattice vibrations to the specific heat of a metal is

$$\begin{aligned} (C_V)_{\text{lattice}} &= 3\,Nk\,[1 - (1/20)\,(T_D/T)^2 + \ldots] && \text{for } T \gg T_D \\ &= (12\pi^4/5)\, Nk\,(T/T_D)^3 && \text{for } T \ll T_D \end{aligned} \tag{8.3.8}$$

where T_D is the Debye temperature of metal, which is around 100 to 400K. At ordinary temperatures, the specific heat of the free electrons in metal is negligible in comparison to the specific heat of the lattice. At very low temperature, when the Debye T^3 law is valid, the contribution of the free electrons is observable. Thus, at low temperatures, the total specific heat of a metal is given by

$$C_V = (\pi^2/2)\, Nk\, (T/T_F) + (12\pi^4/5)\, Nk\, (T/T_D)^3 = \gamma T + \beta T^3 \qquad (8.3.9)$$

where γ and β are constants characteristic of the metal. The variation of C_V/T against T^2 is shown in Fig.8.6. The results are in good agreement with the experimental values. At sufficiently low temperatures, the linear term predominates, and this allows one to determine the electronic specific heat term from the experiment. The intercept gives the value of γ, while the value of β can be determined from the slope of the curve. However, the theoretical γ does not agree with experimental values. The ratio of γ_{exp} and γ_{theor} is generally given by the relation

$$\gamma_{exp}/\gamma_{theor} = m^*/m \qquad (8.3.10)$$

where m^* is the thermal effective mass. The value of γ_{exp} is found to be greater than γ_{theor}. This difficulty is a consequence of the over-simplifying assumptions made in the free electron model.

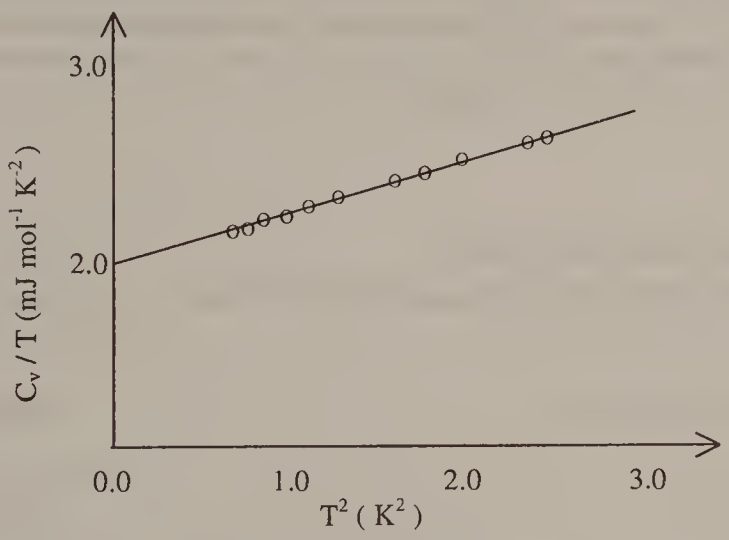


Fig.8.6. Low temperature specific heat of metal, C_V/T as a function of T^2. Experimental values of potassium are shown by circle.

8.4. Thermionic Emission

As discussed in the previous section, free electron in a metal move freely through the volume of the metal. These electrons repel each other by the coulomb repulsion, which is balanced by the attraction from the positively charged ions. Electrons must be contained within the metal by a suitable potential. At absolute zero, the energy distribution of these electrons varies from zero to Fermi energy $\in_F$. However at this temperature no electron can escape from the metal to vacuum, since the electrons are unable to overcome the surface potential barrier in this situation. When the temperature is raised, a finite but very small fraction of electrons acquire energy greater than Fermi energy $\in_F$. These electrons may escape the metal surface overcoming the surface potential. The number of electrons leaving the

surface per sec. increases with increase of temperature of the emitter. Thus metals emit electrons when heated to a high temperature. This phenomenon is known as 'thermionic emission'.

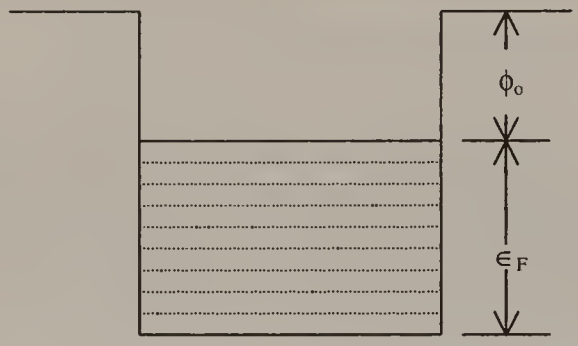


Fig.8.7. Electronic energy states of metal for thermionic emission

When the metal is at absolute zero of temperature, it requires an energy ϕ_o to remove the electron from the Fermi level as shown in Fig.8.7. Let us consider an emitting metal whose emitting surface is plane and perpendicular to the x-axis in a vacuum. The free electrons in metal move with different momenta in different directions. Only those electrons may leave the metal surface in the x-direction, whose velocities exceed the critical velocity v_x^0 given by the relation

$$\phi_o = p_x^{0^2}/2m$$

where $p_x^0 = mv_x^0$ and ϕ_o is the characteristic constant of the metal.

The number of electrons per unit volume in the momentum range p_x, p_x+dp_x, p_y, p_y+dp_y and p_z, p_z+dp_z is given by

$$\rho(p)\, dp_x\, dp_y\, dp_z = (2/h^3)\, dp_x dp_y dp_z/(\exp(x)+1) \tag{8.4.1}$$

where

$$x = ([(p_x^2 + p_y^2 + p_z^2)/2m] - \mu)/kT \tag{8.4.2}$$

The number of electrons per unit volume having the momentum component between p_x and $p_x + dp_x$ is obtained by integrating over p_y and p_z. Thus

$$\rho(p_x)\, dp_x = dp_x \int_{-\infty}^{\infty} dp_y \int_{-\infty}^{\infty} dp_z\, \rho(p) \tag{8.4.3}$$

Hence the number of electrons striking normally per unit area of the surface per second is given by

$$dN = v_x\, \rho(p_x)dp_x = (p_x/m)\, \rho(p_x)dp_x \tag{8.4.4}$$

If we assume that every electron with $p_x > (2m\phi_o)^{1/2}$ leaves the metal surface, then the total number of electrons emitted per second from the unit area of the metal surface is given by

$$N = \int_{p_x^0}^{\infty} (p_x/m)\rho(p_x)dp_x$$

$$= (2/mh^3) \int_{-\infty}^{\infty} dp_y \int_{-\infty}^{\infty} dp_z \int_{p_x^0}^{\infty} p_x dp_x/(\exp(x) + 1) \tag{8.4.5}$$

where $p_x^0 = (2m\phi_o)^{1/2}$ and the chemical potential μ appearing in (8.4.2) is a function of T. For the temperature at which the thermionic emission takes place, $\exp(x) >> 1$, consequently one can neglect unity in comparison with $\exp(x)$ in (8.4.5). Under these conditions (8.4.5) can be written as

$$N = (2/mh^3) \int_{-\infty}^{\infty} \exp(-p_y/2mkT)\, dp_y \int_{-\infty}^{\infty} \exp(-p_z^2/2mkT)dp_z \int_{p_x^0}^{\infty} \exp(-[(p_x^0/2m) - \mu]/kT)\, p_x dp_x \tag{8.4.6}$$

Evaluation of the first two integrals is simple, having the value as

$$\int_{-\infty}^{\infty} \exp(-p_y/2mkT)dp_y = (2\pi mkT)^{1/2}$$

In order to evaluate the last integral, we put

$$(p_x^2/2m) - \mu = y$$

then

$$\int_{p_x^0}^{\infty} \exp(-[(p_x^2/2m) - \mu]/kT)\, p_x dp_x = \int_{\phi/kT}^{\infty} \exp(-x)\, dx = (mkT)\exp(-\phi/kT)$$

where $\phi = (p_x^{02}/2m) - \mu = \phi_0 - \mu$.

Substituting these values in (8.4.6), we get

$$N = (4\pi m/h^3)k^2T^2 \exp(-\phi/kT) \tag{8.4.7}$$

Then the thermionic current density I is expressed as

$$I \equiv Ne = (4\pi me/h^3)k^2T^2 \exp(-\phi/kT) \tag{8.4.8}$$

where e is the charge of an electron. It can be written in the form

$$I = AT^2 \exp(-\phi/kT) \tag{8.4.9}$$

where

$$A = 4\pi mek^2/h^3$$

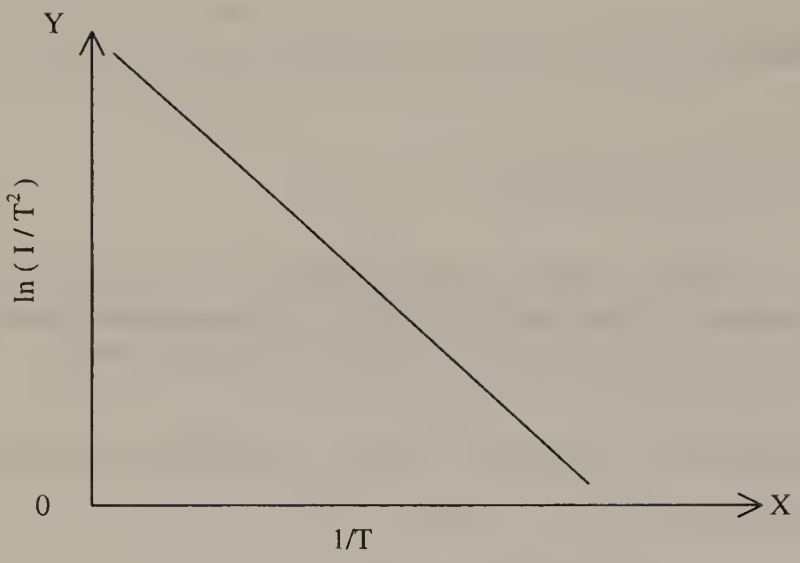


Fig.8.8. A graph of ln (I/T^2) as a function of 1/T.

Eq.(8.4.9) is known as the Richardson-Dushman equation for thermionic emission. A graph of ln(I/T^2) as function of (1/T) is shown in Fig.8.8 which is a straight line having negative slope ϕ/k and intercept equal to A.

8.5. Photoelectric Emission

When a photon of energy hν is incident on a metal plate, it is absorbed by a conduction electron, which escapes from the surface as photoelectron as schematically shown in Fig.8.9. A part of its energy ϕ_0, known as the work function, is used up in liberating the electron from the metal surface and other part $\frac{1}{2} mv^2$ is used in imparting velocity v to the ejected electron, so that

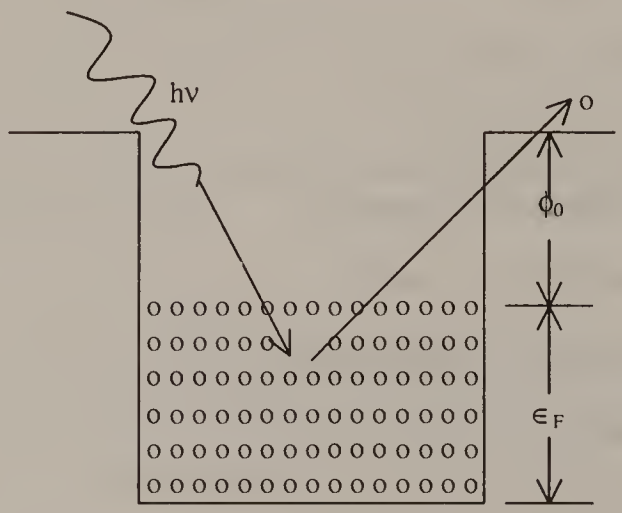


Fig.8.9. Photo electric emission in metal

$$(1/2)\, mv^2 = h\nu - \phi_0 = h\nu - h\nu_0$$

where ν_0 is called the 'threshold frequency'.

The emitting metal just like thermionic emission, is assumed to be in a vacuum with the emitting surface plane and perpendicular to the x-axes. We further assume that momentum components p_y and p_z remain unchanged and only those electrons escape for which

$$p_x \geq p_x^{02} = (2m[\phi_0 + \mu - h\nu])^{1/2}$$

Let α be the probability that some electrons absorb photons to satisfy this condition. The number of electrons having the momentum component lying between p_x and $p_x + dp_x$ striking unit area of the surface per second is

$$dN = \alpha(2/h^3)\,(p_x/m)dp_x \int_{-\infty}^{\infty}\int dp_y dp_z/(\exp(x)+1) \tag{8.5.1}$$

where

$$x = ([(p_x^2 + p_y^2 + p_z^2)/2m] - \mu)/kT \tag{8.5.2}$$

Transforming to the cylindrical coordinates p_x, r, ϕ where

$$r^2 = p_y^2 + p_z^2$$

and

$$dp_y\, dp_z = r\, dr\, d\phi$$

we can write (8.5.1) as

$$dN = \alpha(2/h^3)\,(p_x/m)dp_x \int_0^{2\pi} d\phi \int_0^{\infty} rdr/(C\exp(r^2/2mkT)+1)$$

$$= \alpha(4\pi/h^3)\,(p_x/m)dp_x \int_0^{\infty} rdr/(C\exp(r^2/2mkT)+1) \tag{8.5.3}$$

where

$$C = \exp([(p_x^2/2m) - \mu]/kT) \tag{8.5.4}$$

(8.5.3.) can be rewritten as

$$dN = \alpha(4\pi/h^3)\,(p_x/m)dp_x \int_0^{\infty} \exp(-r^2/2mkT)rdr/(\exp(-r^2/2mkT)+C)$$

which can be integrated to give

$$dN = \alpha(4\pi/h^3)(mkT)(p_x/m)dp_x \ln[(1+C)/C]$$

$$= \alpha(4\pi/h^3)(mkT)(p_x/m)dp_x \ln[\exp([\mu - (p_x^2/2m)]/kT) + 1]$$

Hence the total number of electron N emitted per second from the unit area of the metal surface is given by

$$N = \alpha(4\pi/h^3)(mkT)\int_{p_x^0}^{\infty} dp_x\,(p_x/m)dN \tag{8.5.6}$$

Changing the variable of integration from p_x to

$$t = (p_x^2 - p_x^{0^2}) / 2mkT = [(p_x^2/2m) - \phi_0 - \mu + h\nu] / kT$$

(8.5.6) can be written as

$$N = \alpha(4\pi/h^3)(mkT)(kT)\int_0^{\infty} dt \ln\{1 + \exp[\gamma - t]\} \tag{8.5.7}$$

where

$$\gamma = (h\nu - \phi_0)/kT$$

The photocurrent I is obtained by multiplying N by the charge e. Thus

$$I = \alpha(4\pi me/h^3)(kT)^2 F(\gamma) \tag{8.5.8}$$

where

$$F(\gamma) = \int_0^{\infty} dt \ln\{1 + \exp[\gamma - t]\} \tag{8.5.9}$$

In order to solve the integral, we put

$$\omega = \exp(\gamma - t)$$

then (8.5.9) can be expressed as

$$F(\gamma) = \int_0^{\omega_0} (d\omega/\omega) \ln(1 + \omega) \tag{8.5.10}$$

where $\omega_0 = e^{\gamma}$. We evaluate this integral in two cases:

(i) when $\gamma < 0$ (i.e. $h\nu < \phi_0$), we evaluate the integral (8.5.10) as

$$F(\gamma) = \int_0^{\omega_0} (d\omega/\omega)\{\omega - (\omega^2/2) + (\omega^3/3) - \ldots\}$$

$$= \omega_0 - (\omega_0^2/2^2) + (\omega_0^3/3^2) - \ldots$$

$$= e^{\gamma} - (e^{2\gamma}/2^2) + (e^{3\gamma}/3^2) - \ldots$$

(ii) when $\gamma > 0$ (i.e. $h\nu > \phi_0$), we write (8.5.10) as

$$F(\gamma) = \int_0^1 (d\omega/\omega) \ln(1+\omega) + \int_1^{\omega_0} (d\omega/\omega) \ln(1+\omega)$$

$$= \int_0^1 (d\omega/\omega) \ln(1+\omega) + \int_1^{\omega_0} (d\omega/\omega) \ln\omega + \int_1^{\omega_0} (d\omega/\omega) \ln(1+(1/\omega)) \quad (8.5.12)$$

evaluating each integral separately, we get the results as

$$F(\gamma) = (\pi^2/6) + (\gamma^2/2) - [e^{-\gamma} - (e^{-2\gamma}/2^2) + (e^{-3\gamma}/3^2) - \ldots] \quad (8.5.13)$$

So the photocurrent I becomes

$$I = \alpha(4\pi mek^2/h^3)T^2 F((h\nu - \phi)/kT) \quad (8.5.14)$$

This is known as the Fowler equation for the photoelectric current for the value of ν near the threshold frequency, It can be written in a general form

$$I = AT^2 F(\gamma) \quad (8.5.15)$$

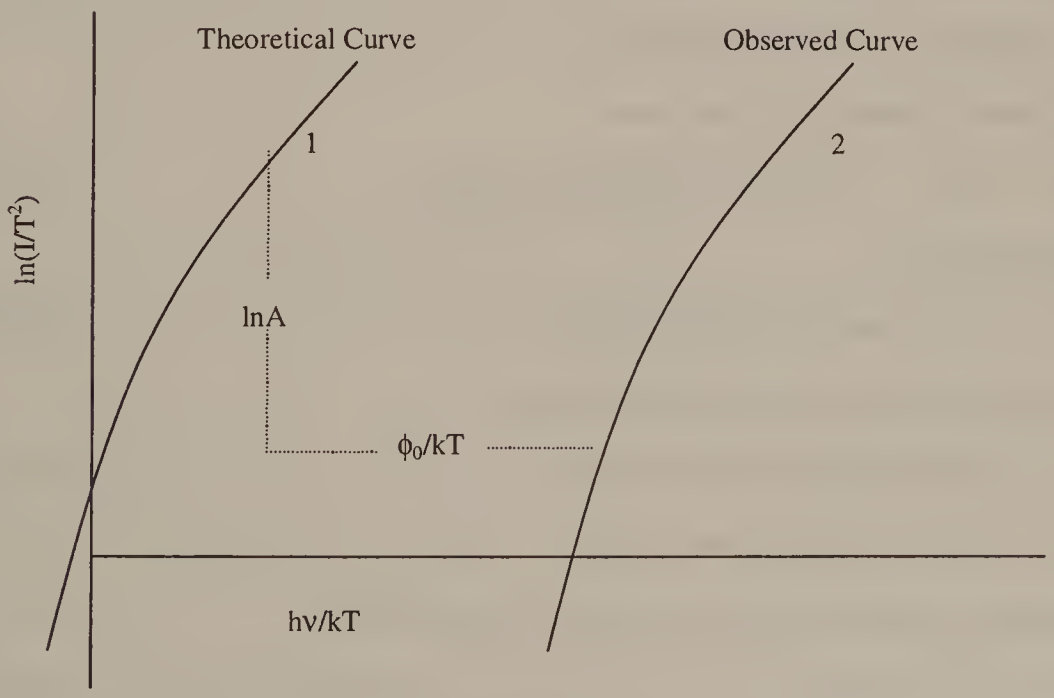


Fig.8.10. A graph of $\log(I/T^2)$ as a function of $h\nu/kT$

$F(\gamma)$ is a universal function of γ, whose form is same for all metals and all temperatures. The curve of $\ln(I/T^2)$ as a function of $h\nu/kT$ is called the Fowler plot and shown in Fig.8.10. When the observed

curve (2) is shifted horizontally by an amount ϕ_0/kT and vertically by an amount by lnA, it will coincide with the theoretical curve(1). The horizontal shift determines ϕ_0 and hence the true threshold frequency ν_0.

8.6. Saha Theory of Thermal Ionization

When a substance is heated to a high temperature, electrons are knocked off and atoms get ionized. We consider a simple case of thermal ionization of an atom into the ion and a free electron. We can represent the process of ionization by the relation

$$A \quad A^+ + e^- \tag{8.6.1}$$

We assume the free atoms, ions and electrons as perfect gases. The Helmholtz free energy of gas of free atoms is given by (see Eq.6.14.6)

$$A_a = -NkT \ln[(ev/N)(2\pi M_a kT/h^2)^{3/2} q_a(T)] \tag{8.6.2}$$

where M_a is the mass of an atom A and $q_a(T)$ is the single-particle partition function corresponding to the internal motion. For free atoms the only internal states are the electronic states. At high temperature, $q_a(T)$ can be written as

$$q_a(T) = g_a \exp(-\epsilon_a/kT) \tag{8.6.3}$$

where g_a is the degeneracy with the energy level ϵ_a.

Then the Gibbs free energy for the free atoms is

$$G_a = A_a + P_a V = -NkT \ln[(V/N)(2\pi M_a kT/h^2)^{3/2} q_a(T)] \tag{8.6.4}$$

and the chemical potential

$$\mu_a = -kT \ln[(2\pi M_a kT/h^2)^{3/2} (kT/p_a) q_a(T)] \tag{8.6.5}$$

Similarly the chemical potential for the ions and electrons

$$\mu_i = -kT \ln[(2\pi M_i kT/h^2)^{3/2} (kT/p_i) q_i(T)] \tag{8.6.6}$$

$$\mu_e = -kT \ln[(2\pi m_e kT/h^2)^{3/2} (kT/p_e) q_e(T)] \tag{8.6.7}$$

where M_i and m_e are, respectively, the mass of an ion and an electron, and

$$q_i(T) = g_i \exp(-\epsilon_i/kT) \tag{8.6.8a}$$

$$q_e(T) = g_e \exp(-\epsilon_e/kT) \tag{8.6.8b}$$

Here g_i and g_e are, respectively, the degeneracies of ions and electrons with energies ϵ_i and ϵ_e. Let ϵ^* be the ionization energy, then

$$\epsilon^* = \epsilon_i + \epsilon_e - \epsilon_a$$

According to the Laws of thermodynamics the total change in the chemical potential of the system is zero, that is

$$\mu_i + \mu_e - \mu_a = 0 \tag{8.6.9}$$

Substituting the values of the chemical potentials in (8.6.9), we get

$$\ln (P_i P_e/P_a) = \ln [(2\pi/h^2)^{3/2} (kT)^{5/2} (M_i m_e/M_a)^{3/2} (g_i g_e/g_a) \exp(-\epsilon^*/kT)]$$

Then the equilibrium constant is

$$K_P(T) = P_i P_e/P_a = (2\pi/h^2)^{3/2} (kT)^{5/2} (M_i m_e/M_a)^{3/2} (g_i g_e/g_a) \exp(-\epsilon^*/kT) \tag{8.6.10}$$

Since the electronic mass is 10^{-4} times the atomic mass, so M_i/M_a 1. Further for electron with spin ½, g_e=2. Then (8.6.10) becomes

$$K_P(T) = P_i P_e/P_a = (2\pi m_e/h^2)^{3/2} (kT)^{5/2} (2g_i/g_e) \exp(-\epsilon^*/kT) \tag{8.6.11}$$

When neutral atoms are heated, some atoms are ionised, then the number of ions equal to the number of electrons and so

$$P_i = P_e$$

and

$$P = P_a + P_i + P_e$$

Then

$$P_i P_e/P_a = P_e^2/(P-2P_e) = P(P_e/P)^2/ (1 - 2(P_e/P))$$

Let us assume that we heat n gm-mol of A per unit volume and let x mole fraction be ionized, then we have

$$P_i = P_e = nxkT$$

$$P_a = n(1 - x)kT$$

and

$$P = P_a + P_i + P_e = n(1 + x)kT$$

Hence we have

$$P_i = P_e = (x/(1 + x))\, P$$

$$P_a = ((1 - x)/(1 + x))\, P$$

Then (8.6.11) reduces to

$$(x^2/(1-x^2))P = (2\pi m_e/h^2)^{3/2} (kT)^{5/2} (2g_i/g_a) \exp(-\epsilon^*/kT) \tag{8.6.12}$$

Using the relation $P = n(1+x)kT$, Eq.(8.6.12) can be written as

$$(x^2/(1-x))n = (2\pi m_e k/h^2)^{3/2} (2g_i/g_a) T^{3/2} \exp(-\epsilon^*/kT) \quad (8.6.13)$$

which can be expressed in a form

$$\ln n = A + (3/2) \ln T - \epsilon^*/kT \quad (8.6.14)$$

where

$$A = \ln [(2\pi m_e k/h^2)^{3/2} (2g_i/g_a) ((1-x)/x^2)] \quad (8.6.15)$$

Eq.(8.6.12) was first derived by Saha in 1920 and applied to explain the ionization in the solar chromosphere. Now a days it has a wide applications in plasma studies and ionization process in semiconductors.

8.7. Statistical Model of Atom

An interesting application of the Fermi-Dirac statistics was made for calculating the electron distribution in the extra nuclear space of a heavy atom. An atom contain nucleus surrounded by electrons. Inside a nucleus of atomic weight A and atomic number Z, there are Z protons and (A-Z) neutrons. Both protons and neutrons are collectively called nucleons. Thus there are A nucleons in the nucleus, surrounded by Ne = Z electrons. Both protons and neutrons are fermions of spin s=½ obeying the Fermi-Dirac statistics. There are very strong attractive forces between the nucleons inside the nucleus. However, we roughly assume that the protons and neutrons are two independent ideal fermion gases.

The Fermi energy ϵ_F and the Fermi temperature T_F of an ideal neutron gas is given by

$$\epsilon_F^n = (\hbar^2/2m) (6\pi^2 N/gV)^{2/3} = kT_F \quad (8.7.1)$$

where N is the number of neutrons, each of mass m, in a volume V and g = 2s+1=2. In this case V is the volume of the atomic nucleus. If R be the radius of a nucleus of atomic weight A, then experimentally it is found that $R = 1.3 \times 10^{-15} A^{1/3}$ metre. The concentration of neutrons in the nucleus is

$$N/V = (A-Z)/V = (A-Z)/(4\pi/3)R^3 = 1.087 \times 10^{44}((A-Z)/A) \text{ metre}^{-3}$$

Substituting the values of N/V, m and $\hbar$ in (8.7.1), the Fermi energy of an ideal neutron gas is obtained as

$$\epsilon_{F.}^n = 4.56 \times 10^{-22} \text{ J} = 28.5 \text{ MeV}$$

and corresponding Fermi temperature is

$$T_F = 3.31 \times 10^{11} \text{ K}$$

This shows that the ideal neutron is degenerate.

For a light nucleus, Z = N, so that for light nucleus, the concentration and hence Fermi energy for the proton is same as that of the neutrons. For A>100, there are more neutrons than protons in a nucleus, so that the Fermi energy for proton is less than that for the neutrons.

Next we consider the electron distribution around the nucleus in a heavy atom. We consider the electrons in this system as a completely degenerate Fermi gas of non-uniform density $n(\mathbf{r})$ in the field of the electric potential $\phi(r)$.

In this system we have two electrons (with opposite spins) with $P < P_F$, where P_F is the Fermi momentum of electron gas, given by

$$P_F(\mathbf{r}) = \sqrt{(2m\in_F)} = (3\pi^2 n(r))^{1/3}\hbar \tag{8.7.2}$$

Here $P_F(\mathbf{r})$ is a function of $\mathbf{r}$, since the electron density varies from point to point.

The total energy ε of an electron at the top of the Fermi sea at the point $\mathbf{r}$ is given by

$$\varepsilon(\mathbf{r}) = (1/2m_e)\, P_e^2(\mathbf{r}) - e\phi(\mathbf{r}) \tag{8.7.3}$$

where m_e is the mass and e the charge of the electron. At the boundary of the system, $\varepsilon(\mathbf{r}) = 0$ for all $\mathbf{r}$

$$(1/2m_e)\, P_e^2(\mathbf{r}) - e\phi(\mathbf{r}) = 0 \tag{8.7.4}$$

From (8.7.3) and (8.7.4), we get

$$n(\mathbf{r}) = ((2m_e e)^{3/2}/3\pi^2\hbar^3)\,(\phi(\mathbf{r}))^{3/2} \tag{8.7.5}$$

Substituting this value of $n(\mathbf{r})$ in the Poisson equation

$$\nabla^2\phi(\mathbf{r}) = -4\pi\rho(\mathbf{r}) = 4\pi e n(\mathbf{r}) \tag{8.7.6}$$

We obtain

$$\nabla^2\phi(\mathbf{r}) = (4e(2m_e e)^{3/2}/3\pi\hbar^3)\,(\phi(\mathbf{r}))^{3/2} \tag{8.7.7}$$

Assuming $\phi(\mathbf{r})$ as a function of r only, (8.7.7) can be expressed in the form

$$(1/r^2)(d/dr)\,[r^2(d/dr)\,\phi(\mathbf{r})] = (4e(2m_e e)^{3/2}/3\pi\hbar^3)\,(\phi(\mathbf{r}))^{3/2} \tag{8.7.8}$$

This is known as the Thomas-Fermi equation of the system. In order to solve this equation, we introduce dimensionless variable x and Φ defined as

$$x = 2\,(4/3\pi)^{2/3}\,(m_e e^2/\hbar^2)\,Z^{1/3}\,r = (Z^{1/3}/0.8853a_B)r \tag{8.7.9}$$

and

$$\Phi(x) = \phi(r)/(Ze/r) \tag{8.7.10}$$

where Ze/r is the unscreen coloumb potential and $a_B = me^2/\hbar^2$ the first Bohr radius of the hydrogen atom. Then (8.7.8) reduces to

$$d^2\Phi/dx^2 = \Phi^{3/2}/x^{1/2} \tag{8.7.11}$$

This is the dimensionless Thomas-Fermi equation. Its solution is guided by the condition (i) when $r \to 0$, $\Phi(r) \to Ze/r$ and (ii) when $r \to r_0$, $\Phi(r) \to 0$. Accordingly the following boundary conditions are employed to solve the equation:

$$\Phi(x) = 1, \qquad \text{when } x \to 0$$

$$\Phi(x) = 0, \qquad \text{when } x \to x_0$$

Further the initial slope of the function is also needed for the solution. Choosing the boundary to be at infinity ($r_0=\infty$), the initial slope of the function $\Phi(x)$ will be -1.5886. Hence $\Phi(x)$ near the origin is given as

$$\Phi(x) = 1 - 1.5886x + (4/3)\, x^{3/2} + \ldots \tag{8.7.12}$$

and for $x \to \infty$

$$\Phi(x) = 144/x^3$$

The general solution of (8.7.11) can be obtained numerically, which shows that $\Phi(x)$ is a monotonically decreasing function of x

From (8.7.10), we obtain the electric potential $\phi(r)$

$$\phi(r) = (Ze/r)\, \Phi(Z^{1/3}r/0.8853a_B) \propto Z^{4/3} \tag{8.7.13}$$

and hence the electron density n(r) from (8.7.5)

$$n(r) \propto Z^2 \tag{8.7.14}$$

Now the mean kinetic energy of an electron at the point r will be

$$\langle \varepsilon(n) \rangle = (3/5)\, \epsilon_F(r) = (3/5) e\phi(r) \propto Z^{4/3}$$

Thus the mean energy per electron is proportional to $Z^{4/3}$. Accordingly, the mean de Broglie wavelength λ of the electrons in the cloud, which is given by

$$\lambda = h/(2m\langle \varepsilon \rangle)^{1/2} = h/((6/5)me\phi(r))^{3/2}$$

will be proportional to $Z^{-2/3}$. From (8.7.7) it is clear that the distance r over which the functions $\phi(r)$ and n(r) undergo significant variations, is proportional to $Z^{-1/3}$. Thus we find that the Thomas-Fermi model is more appropriate for heavier atoms ($Z^{-2/3} << Z^{-1/3}$).

8.8. Relativistic Degenerate Electron Gas

We now consider the degenerate electron gas when the Fermi momentum of the electron gas is comparable with the characteristic momentum mc of an electron (where m is the rest mass of an electron and c is the velocity of light). In this situation, the dynamics of the electron is relativistic and the energy-momentum relationship for a relativistic particle is

$$\epsilon = \sqrt{(c^2p^2 + m^2c^4)} \tag{8.8.1}$$

instead of non-relativistic relation

$$\epsilon = p^2/2m$$

The number of quantum states in the momentum range p and p+dp is given by

$$g(p)\,dp = (2\pi gV/h^3)\,p^2dp \tag{8.8.2}$$

where g = 2 for electron.

The electron gas obeys the Fermi-Dirac statistics. In this case the electrons will be distributed among the various quantum states according to Pauli's exclusion principle. For simplicity, we consider the electron gas in the state of (almost) complete degeneracy. In such a case, all the single particle states up to $\epsilon = \epsilon_F$ are completely filled with one particle per state while all the single particle states with $\epsilon > \epsilon_F$ are empty. Let P_F be the Fermi momentum corresponding to the Fermi energy ϵ_F. They are related by Eq.(8.8.1) in this case.

The total number of electrons in the gas is given by

$$N = (4\pi gV/h^3)\int_0^{P_F} p^2dp = (4\pi gV/3h^3)\,P_F^3 \tag{8.8.3}$$

so that the Fermi momentum P_F is

$$P_F = (3N/4\pi gV)^{3/2}h = (3\rho/4\pi g)^{1/3}h \tag{8.8.4}$$

and the Fermi energy ϵ_F is

$$\epsilon_F = c\sqrt{(P_F^2 + m^2c^2)} = mc^2\cosh(P_F/mc) = mc^2\cosh[(3\rho/4\pi g)^{1/3}(h/mc)] \tag{8.8.5}$$

The total energy of the system is

$$U = (4\pi gVc/h^3)\int_0^{P_F} (p^2 + m^2c^2)^{1/2}\,p^2dp$$

$$= (4\pi gVc/h^3)(mc)^4\int_0^{P_F/mc} (1 + X^2)^{1/2}\,X^2dX \tag{8.8.6}$$

In order to solve the integral appearing in Eq.(8.8.6), we put $X = \sinh\theta$, then

$$U = (4\pi gVc/h^3)\,(mc)^4\,(1/8)\int_0^{\sinh^{-1}(P_F/mc)} [\cosh(4X) - 1]\,d\theta$$

$$= (\pi gVc/8h^3)\,(mc)^4\,[\sinh(4X_F) - 4X_F] \tag{8.8.7}$$

where $X_F = \sin^{-1}(P_F/mc)$.

Alternatively, it can be expressed as

$$U/V = (\pi gc/2h^3)\,[P_F\,(2P_F^2 + m^2c^2)\,(P_F^2 + m^2c^2)^{1/2} - (mc)^4 \sinh^{-1}(P_F/mc)] \tag{8.8.8}$$

The pressure of the gas is

$$P = -(\partial U/\partial V)_{S=0}$$

$$= (\pi gc/2h^3)\,[P_F\,((2/3)P_F^2 - m^2c^2)\,(P_F^2 + m^2c^2)^{1/2} + (mc)^4 \sinh^{-1}(P_F/mc)] \tag{8.8.9}$$

Let us consider a specific case, when the energy of a particle is large compared with the rest energy mc^2. In this case (8.8.1) takes the form

$$\epsilon = cp \tag{8.8.10}$$

Then Fermi energy ϵ_F is given by

$$\epsilon_F = c\,P_F = (3\rho/4\pi g)^{1/3}\,ch \tag{8.8.11}$$

Neglecting m^2c^2 terms in (8.8.8), the total energy is given by

$$U = (\pi gVc/h^3)\,P_F^4 \tag{8.8.12}$$

or

$$U = (3/4)\,NcP_F = (3/4)\,(3/4\pi g)^{1/2}\,chN(N/V)^{1/3} \tag{8.8.13}$$

The pressure of the gas is obtained from (8.8.9) as

$$P = (1/3)\,(\pi gc/h^3)\,P_F^4 = (1/3)(U/V) = (1/4)\,(3/4\pi g)^{1/3}\,ch\rho^{4/3} \tag{8.8.14}$$

Thus the pressure of an extreme relativistic electron gas at absolute zero temperature is proportional to the 4/3 power of density.

We now consider an extreme relativistic degenerate electron gas at finite temperature. The number of quantum states with the energy range ϵ and $\epsilon+d\epsilon$ is obtained from Eqs.(8.8.2) and (8.8.10) as

$$g(\epsilon)d\epsilon = (4\pi gV/c^3h^3)\,\epsilon^2 d\epsilon \tag{8.8.16}$$

The total number of particles in the gas is given by

$$N = (4\pi gV/c^3h^3)\int_0^\infty \epsilon^2 d\epsilon/(\exp[(\epsilon-\mu)/kT]+1)$$

$$= (4\pi gV/c^3h^3)\,F_3(z) \tag{8.8.17}$$

where $F_n(z)$ is given by Eq.(8.2.18).

From (8.8.11) and (8.8.17), we obtain an expression for μ

$$\mu \quad \epsilon_F [1 - (\pi^2/3)(T/T_F)^2 + \ldots], \; T \ll T_F \tag{8.8.18}$$

The total energy of the system in this case is given by

$$U = (4\pi gV/c^3h^3) \int_0^\infty \epsilon^2 d\epsilon /(\exp[(\epsilon - \mu)/kT] + 1)$$

$$= (5\pi gV/c^3h^3) F_4(z) \tag{8.8.19}$$

With the help of Eqs.(8.8.11) and (8.8.19), we get

$$U = (3/4)N\epsilon_F [1 + (2\pi^2/3) (T/T_F) + \ldots] \tag{8.8.20}$$

and specific heat of the relativistic electron gas becomes

$$C_V = \pi^2 Nk (T/T_F) \tag{8.8.21}$$

The thermodynamic potential Ω of the system is

$$\Omega = \sum_i \Omega_i = kT \sum_i \ln (1 + \exp ((\mu - \epsilon_i)/kT)].$$

The summation can be transformed into the integral, then an expression for the thermodynamic potential Ω is given by

$$\Omega = (4\pi gV(kT)/c^3h^3) \int_0^\infty d\epsilon \; \epsilon^2 \ln [1 + \exp((\mu - \epsilon)/kT)]$$

Integrating by parts, we get

$$\Omega = -(1/3) (4\pi gV/c^3h^3) \int_0^\infty \epsilon^3 d\epsilon \; / (\exp[(\epsilon - \mu)/kT] + 1)$$

$$= -(1/3) U \tag{8.8.22}$$

Using the relation $\Omega = -PV$, we have

$$PV = (1/3)U \tag{8.8.23}$$

Thus this relation is valid for an extreme relativistic electron gas for all temperatures.

Substituting Eq.(8.8.20) in Eq.(8.8.23), the pressure of the system is given by

$$P = (1/4) (N\epsilon_F/V) [1 + (2\pi^2/3) (T/T_F) + \ldots] \tag{8.8.24}$$

The first term is the ground state value of the pressure for the extreme relativistic electron gas and the second is the correction arising due to rise in temperature.

8.9. Theory of White Dwarf Stars

The most important and interesting application of the Fermi-Dirac statistics is the white dwarf stars-small stars which are abnormally faint for their white colour. The white dwarf stars are an outcome of stellar evolution. It is an established fact that the source of an enormous amount of energy of a star is the continuous process of fusion inside the star of hydrogen to form helium. During the process of continuous fusion inside the star, the outward pressure generated is so great that it outbalances the inward gravitation force. Consequently, the star continuously expands till it consumes much of its nuclear fuel and a star of the type known as the red giant is evolved. When the nuclear fuel inside the star is completely used up, the outward pressure is not sufficient enough to balance the inward gravitational force. Hence the star begins to collapse under its own gravitational force. Finally it will reach a stage in the stellar evolution which is known as white dwarf. The density at this stage becomes so great that it gives rise to an effective pressure, strong enough to prevent further contraction of the body. Many such white dwarfs have been observed. A typical white dwarf is Sirius B, with the following estimated data:

$$\text{mass} = 2.09 \times 10^{30} \text{ kg}$$

and

$$\text{radius} = 5.57 \times 10^{3} \text{ km}$$

For comparison, the radii of the earth and the sun are 6.4×10^3 km and 7.0×10^5 km, respectively.

A detailed study of the constitution of white dwarf stars reveals that they lack brightness, because the hydrogen contents are more or less used up. They are composed mostly of helium. Whatever light brightness they have, it is derived from the gravitational energy, which is related through a slow contraction of the star.

An idealised model of a white dwarf star have the central temperature 10^7 K, which corresponds to a mean thermal energy of the order of 10^3 eV. Hence the helium atoms are expected to be completely ionised. Thus the white dwarf star may be regarded as a gas composed of helium nuclei and electrons as well as radiation. However, we may neglect the presence of the helium nuclei and radiation in the system and regard the star as a gas of electrons with a density of the order of 10^{36} electrons/m^3. This obeys the Fermi-Dirac statistics.

Let N be the number of free electrons in the white dwarf star, then the number of nucleons in the star is N_p=2N. Let M and V be the mass and volume respectively of the star of radius R, then

$$M = N(m_e + 2m_p) \quad 2Nm_p$$

$$V = (4\pi/3)\, R^3 \tag{8.9.1}$$

where m_e and m_p are the masses of an electron and a proton, respectively. Since the density of electrons is very large, the Fermi momentum P_F is comparable to $m_e c$ of an electron (where c is the velocity of light); the dynamics of the electrons in this case is relativistic. Further, the Fermi temperature T_F is found to be of the order of 10^{10} K, which is much greater than the temperature of the star ($T/T_F \sim 10^{-3}$). Thus we regard the electron gas to be an ideal Fermi gas in a state of (almost) complete degeneracy (i.e. in its ground state). The pressure exerted by the electron gas is counterbalanced by the gravitational attractive force that binds the star. This gravitational force is due, almost entirely, to the helium nuclei in the star. This ideal model shows a remarkable combination of quantum mechanics, relativity and gravitational law.

Let us first calculate the properties of a relativistic electron gas in its ground state; the energy-momentum relationship for a relativistic electron is

$$\epsilon = \sqrt{(c^2p^2 + m_e^2 c^2)} \tag{8.9.2}$$

The total number of electrons (g = 2) is given by

$$N = (8\pi V/h^3) \int_0^{P_F} p^2 dp = (8\pi V/3h^3) P_F^3 \tag{8.9.3}$$

Hence the Fermi momentum P_F is

$$P_F = (3N/8\pi V)^{1/3} h = (3\rho/8\pi)^{1/3} h \tag{8.9.4}$$

We follow the method discussed in Sec.8.8 to calculate energy of the electron gas of the white dwarf star. Thus, the total energy of the electron gas is given by

$$U_e = (8\pi Vc/h^3) \int_0^{P_F} (P^2 + m_e^2 c^2)^{1/2} P^2 dP$$

$$= (8\pi Vc/h^3) (m_e c)^4 \int_0^{\xi_F} (1 + X^2)^{1/2} X^2 dX$$

$$= (\pi Vc/3h^3) (m_e c)^4 A(\xi_F) \tag{8.9.5}$$

where

$$A(\xi_F) = (3/4) [\sinh (4X_F) - 4X_F] \tag{8.9.6}$$

with

$$X_F = \sinh^{-1}(\xi_F)$$

$$\xi_F = P_F/m_e c = (3\rho/8\pi)^{1/3} (h/m_e c) = (9\pi M/8m_p)^{1/3} (h/m_e c) (1/R) \tag{8.9.7}$$

Alternatively, $A(\xi_F)$ can be expressed as

$$A(\xi_F) = 3\xi_F (2\xi_F^2+1) (\xi_F^2+1)^{1/2} - 3 \sinh^{-1} \xi_F \tag{8.9.8}$$

The pressure of the gas is

$$P = -(\partial U/\partial V) = (\pi c(m_e c)^4/3h^3) B(\xi_F) \tag{8.9.9}$$

where

$$B(\xi_F) = [- V (\partial \xi_F/\partial V) (\partial A(\xi_F)/\partial \xi_F) - A(\xi_F)]$$

$$= [\xi_F (\partial A(\xi_F)/\partial \xi_F) - A(\xi_F)]$$

$$= \xi_F (2\xi_F^2 - 3) (\xi_F^2+1)^{1/3} + 3 \sinh^{-1} \xi_F \tag{8.9.10}$$

The functions $A(\xi_F)$ and $B(\xi_F)$ can be evaluated for any value of ξ_F. Their asymptotic values are given as

$$A(\xi_F) = (12/5)\xi_F^5 - (3/7)\xi_F^7 + (1/6)\,\xi_F^9 + \ldots \qquad (\xi_F \ll 1, \text{ nonrelativistic limit})$$

$$= 6\xi_F^4 - 8\xi_F^3 + 6\xi_F^2 - 3(\ln 2\xi_F - (1/4)) + \ldots \quad (\xi_F \gg 1, \text{ extreme relativistic limit}) \qquad (8.9.11)$$

$$B(\xi_F) = (8/5)\xi_F^5 - (4/7)\xi_F^7 + (1/3)\,\xi_F^9 + \ldots \qquad (\xi_F \ll 1, \text{ nonrelativistic limit})$$

$$= 2\xi_F^4 - 2\xi_F^2 + 3\,(\ln 2\xi_F - (7/12)) + \ldots \qquad (\xi_F \gg 1, \text{ extreme relativistic limit}) \qquad (8.9.12)$$

Substituting the values of V and ξ_F, the energy U_e of the electron gas in these extreme limits can be written as

$$U_e = (12/5)\,\gamma\delta^{5/3}(1/R^2) \qquad \text{(Nonrelativistic limit)} \qquad (8.9.13)$$

$$= 6\gamma\,[(\delta^{4/3}/R) - (4/3)\delta + \delta^{2/3}R] \qquad \text{(extreme relativistic limit)} \qquad (8.9.14)$$

where

$$\gamma = (m_e c^2/18\pi)\,(m_e c/\hbar)^3 \qquad (8.9.15)$$

$$\delta = (9\pi M/8m_p)\,(\hbar/m_e c)^3 \qquad (8.9.16)$$

We now consider the condition of equilibrium of the white dwarf star in the light of this model. For simplicity, we assume that mass of the star is uniformly distributed with density ρ. The energy due to the electron gas in the two extreme cases is given by (8.9.13) and (8.9.14).

In the presence of gravitation, the gravitational potential is given by

$$U_{grav} = -(3\alpha/5)\,(GM^2/R) \qquad (8.9.16)$$

where G is the gravitational constant and α is a pure number of the order of unity, whose value depends on the nature of spatial variation of density ρ. Then, the energy of the white dwarf star is

$$U = U_e + U_{grav} \qquad (8.9.17)$$

When the star is in equilibrium, the energy of the star must be minimum i.e.,

$$(\partial U/\partial V) = 0 \qquad (8.9.18)$$

which gives the value of R, where U(R) is minimum and star is stable. Let us discuss the two extreme cases:

(i) when $\xi_F \ll 1$, the energy of star is

$$U(R) = (12/5)\,\gamma\,\delta^{5/3}\,(1/R^2) - (3\alpha/5)\,(GM^2/R) \qquad (8.9.19)$$

Substitution (8.9.19) in (8.9.18) gives

$$R = 8\,\gamma\,\delta^{5/3}/\alpha GM^2 = (1/4\alpha GMm_p^2)\,(9\pi N/4)^{2/3}\,(\hbar^2/m_e)$$

$$= ((9\pi)^{2/3}/8\alpha)\,(\hbar^2/Gm_e m_p^{5/3})M^{-1/3} \qquad (8.9.20)$$

i.e.

$$R \propto M^{-1/3} \qquad (8.9.21)$$

A star will continue to contract under the influence of gravitational force unit U(R) is a minimum, where the radius of the star varies inversely as the 1/3 power of the mass of the star. This condition is valid at low density, i.e. for small M and large R.

(ii) When $\xi_F \gg 1$, the energy of star is

$$U(R) = 6\gamma\,[(\delta^{4/3}/R) - (4/3)\delta + \delta^{2/3}R] - (3\alpha/5)\,(GM^2/R) \qquad (8.9.22)$$

Substituting (8.9.22) in (8.9.18), we obtain the value of R for minimum energy

$$R = \delta^{1/3}\,[1 - (1/10)(\alpha G/\gamma)(M^2/\delta^{4/3})]^{1/2}$$

$$= ((9\pi)^{1/3}/2)\,(\hbar^2/m_e c)^{1/3}\,(M/m_p)^{1/3}[1 - (M/M_0)^{2/3}]^{1/2} \qquad (8.9.23)$$

where

$$M_0 = (3/64)(\pi/\alpha^3)^{1/2}\,(5c\hbar/Gm_p^2)^{3/2}\,m_p \qquad (8.9.14)$$

Thus we find that the radius of the star decreases as its mass increases, and in the limit when $M \to M_0$, $R \to 0$. This formula predicts that no white dwarf star can have a mass greater than M_0. This critical mass M_0 of a white dwarf is generally known as the Chandrasekhar limiting mass. Detailed investigation by Chandrasekhar gives

$$M_0 = 1.4M\check{I} \qquad (8.9.25)$$

where $M\check{I}$ 10^{30} kg is the mass of the sun.

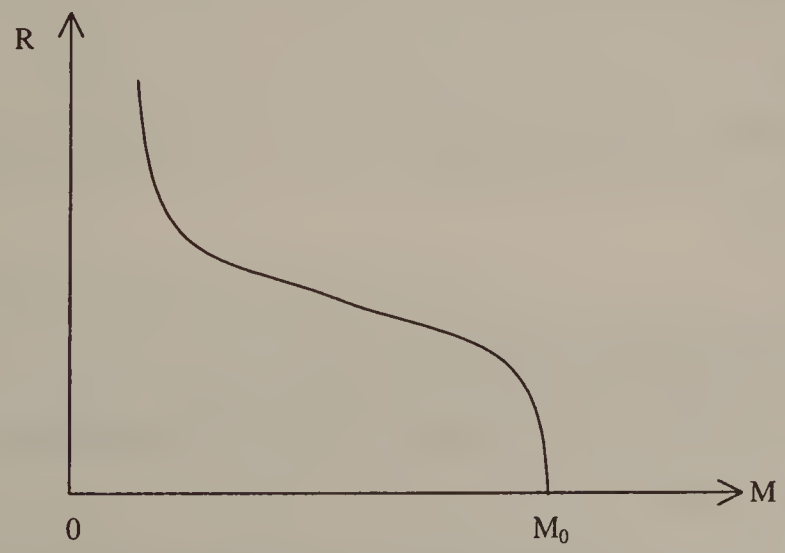


Fig.8.11. The mass-radius relationship for white dwarf stars

The mass-radius relationship of a white dwarf star, obtained from this model, is shown in Fig.8.11, which has been verified by astronomical observations. Thus, according to this model, no star can become a white dwarf unless its mass is less than MǏ. When it will reach a stage of a white dwarf, its further contraction will stop. If the mass of a star is greater than the critical mass, the electron degeneracy pressure is not sufficient to prevent further gravitational collapse of the star.

8.10. Neutron Stars

When the mass of a star is greater than 1.4 MǏ, its contraction will not stop at the white dwarf stage, but the star or a substantial portion of it will collapse further. The inner region falls inward more and more rapidly. The energy set free, goes out as neutrinos and the outer layers fall inward and become sufficiently compact to absorb neutrinos emitted from the core. A shock is generated in the material, just outside the core, resulting in catastrophic explosion which releases energy to form supernova. Supernovas have been observed in our galaxy as well as in other galaxies. The collapsed core of the star at the centre of the rapidly expanding cloud of gas after the supernova explosion consists mainly of neutrons and is called a neutron star. This is very small in comparison to a white dwarf and has very high density. Its density is comparable to the density of proton and neutron. In fact a neutron star can be regarded as an oversized atomic nucleus. The only difference is that the atomic nucleus is bound together by the nuclear forces whereas a neutron star is bound by the gravitational force. A further collapse of neutron star is halted because of Pauli exclusion principle acting on the neutrons which supply the effective forces against the collapse.

For simplicity, we assume that the star consists entirely of neutrons. The neutrons form a fermion gas (with g = 2) obeying Fermi-Dirac statistics. The theory developed for a white dwarf can be extended for a neutron star, provided the mass of the electron m_e, is replaced by the nuclear mass m_p. Let N be the number of neutrons in a star of radium R, then the mass of the star is $M = Nm_p$.

Treating the neutron gas as nonrelativistic, the energy of the neutron gas at T = 0 is

$$U_n = (3N/5)\,(3\pi^2N/V)^{2/3}\,(\hbar^2/2m_p) \tag{8.10.1}$$

$$= (3N/5)\,(9\pi N/4)^{2/3}\,(\hbar^2/2m_p)\,(1/R^2) \tag{8.10.2}$$

and its gravitational potential is

$$U_{grav} = -(3/5)\,(\alpha GM^2/R) = -(3/5)\,(\alpha GN^2m_p^2/R) \tag{8.10.3}$$

The energy of the neutron star is

$$U = U_n + U_{grav} \tag{8.10.4}$$

$$= (3/5)N(9\pi N/4)^{2/3}(\hbar^2/2m_p)(1/R^2) - (3/5)\,(\alpha GN^2m_p^2/R) \tag{8.10.5}$$

The value of R where U(R) is minimum, is obtained from Eq.(8.9.18). Thus, for a neutron star

$$R_n = (\hbar^2/\alpha GNm_p^3)\,(9\pi N/4)^{2/3} \tag{8.10.6}$$

For a neutron star of mass equal to that of the sun we find that the radius is approximately R_n = 12.4 km. The corresponding mass density of a neutron star is 2.5×10^{17} kg/m^3. This is comparable with the

density of nuclear matter. However for more massive neutron star, the relativistic theory must be used. The energy of the neutron star is given by (8.9.22) where

$$\gamma = (m_p c^2/18\pi)\,(m_p c/\hbar)^3 \tag{8.10.7}$$

$$\delta = (9\pi M/4m_p)\,(\hbar/m_p c)^3 \tag{8.10.8}$$

Then the value of R at which U(R) is minimum is obtained from Eq.(8.9.18) as

$$R_n = (9\pi/4)^{1/3}\,(\hbar^2/m_p c)\,(M/m_p)^{1/3}\,[1-(M/M_0)^{2/3}]^{1/2} \tag{8.10.9}$$

where

$$M_0 = (3/16)\,(\pi/\alpha^3)^{1/2}\,(5c\hbar/m_p^2)^{3/2}\,m_p \tag{8.10.10}$$

is the critical mass. The critical mass of the neutron star is estimated to be

$$M_0 = 6.8 M\check{I}$$

where M$\check{I}$ is the mass of the sun. From a more comprehensive investigation, we find that the critical mass of the neutron stars varies in a finite range of masses given below:

$$0.7\,M\check{I} \le M_0 \le 4.0\,M\check{I}$$

The stable configuration of a neutron star can exist only when its mass is less than the critical mass, over which no equilibrium configuration can possibly exist. These higher values of critical mass take into account the presence of heavy subatomic particles called hyperons in addition to ordinary neutrons and protons. Experimental evidence for neutron stars has come from pulsars which are rotating neutron stars.

Stars of masses up to 50 M$\check{I}$ are known to exist. It is evident that such massive stars cannot retain their equilibrium configuration as neutron stars, further collapse will occur. It is very probable that such stars during the collapse or at some earlier stage, throw off much of their material so that their mass could always fall below the limit, required for stable configuration as white dwarf or neutron stars. This is believed to be the case in the Crab Nebula. However, it is evident that stars more massive than about 8.0 M$\check{I}$ cannot retain their equilibrium configuration as neutron stars. For such massive stars whose density exceed that of neutron stars, the force of gravitation becomes so overwhelming that they dominate everything else; and the stars disappear from vision forever. Such stars are known as black holes.

8.11. Magnetic Behaviour of Ideal Electron Gas

In this section, we consider the magnetic behaviour of the free electrons in metal. We have discussed the problem in Sec.6.17 on the basis of Maxwell Boltzmann statistics. However, the electrons having the spin half, obey the Fermi-Dirac statistics. Naturally, if we treat the problem on the basis of the Fermi-Dirac statistics, we obtain significantly different results, especially at low temperatures.

In the presence of the external magnetic field, the free electrons are subjects of two effects: (i) the electrons move in quantised orbits around the direction of field and (ii) the spins of the electrons tend to orient themselves in the direction of the applied magnetic field. The orbital motion of the electrons gives rise to the diamagnetic effect, called Landau diamagnetism, while the orientation of the electron spins gives rise to the paramagnetic effect, called Pauli paramagnetism.

The Hamiltonian of a nonrelativistic free electron in an external magnetic field **B** is given by

$$H = (1/2m)\,(\mathbf{P} + (e/c)\mathbf{A})^2 - \boldsymbol{\mu}.\mathbf{B} \qquad (8.11.1)$$

where **A** is the magnetic vector potential and $\boldsymbol{\mu}$ is the intrinsic magnetic moment operator of an electron of charge e and mass m.

$$\boldsymbol{\mu} = \mu^* \boldsymbol{\sigma} \qquad (8.11.2)$$

$$\mu^* = eh/2mc$$

where $\boldsymbol{\sigma}$ is the Pauli spin operator. The value of μ^* is obtained from the Dirac theory of the electron. The first term of Eq.(8.11.1) gives rise to diamagnetism while the second term is responsible for paramagentism.

Electrons get additional energy $\pm \mu^* B$ in the presence of an external magnetic field **B**. This produces a magnetic moment, resulting in paramagnetism. According to the Boltzmannian treatment, we obtain the Langevin paramagnetism, which has been discussed in Sec.6.17. However, the free electrons in metal may be regarded as a highly degenerate Fermi gas, obeying Fermi-Dirac statistics. The resulting paramagnetism is referred to as the Pauli paramagnetism in contrast to the Langevin paramagnetism.

When electrons move in circular orbits in a magnetic field, they can produce a magnetic moment opposite to the external magnetic field, resulting in diamagnetism. However, if we treat the problem classically, the net magnetic moment produced by the orbital motion is zero. The situation is different when we treat the problem quantum mechanically. We observe diamagnetic effect, which arises from the quantisation of the orbits of the electrons in the presence of an external magnetic field (Landau diamagnetism).

8.12. Pauli Paramagnetism

We consider a system of N (non-interacting) free electrons in the presence of an external magnetic field **B**. Since an electron possesses an intrinsic magnetic moment, the free electrons in metal orient themselves in the direction of the applied magnetic field and make the metal highly paramagnetic. The single particle Hamiltonian in the presence of the magnetic field **B** is

$$H = (p^2/2m) - \boldsymbol{\mu}.\mathbf{B} \qquad (8.12.1)$$

The eigenvalues of $\boldsymbol{\sigma}.\mathbf{B}$ for a fermion of spin $\hbar/2$ are SB, where $S = \pm 1$. Thus the single particle energy levels are

$$\epsilon_{p,S} = (p^2/2m) - S\mu^* B \qquad (8.12.2)$$

where S=+1 and −1 occur for electrons with spin up and spin down, respectively. Thus the free electrons with spin up and spin down have orientation parallel and antiparallel to the magnetic field.

Let N^+ and N^- be the number of electrons with spin up and spin down, respectively, such that

$$N^+ + N^- = N$$

Then the magnetic moment per unit volume due to these electrons is

$$\langle M \rangle = (\mu^*/V)\,(N^+ - N^-) \qquad (8.12.3)$$

We may regard the system as a mixture of two components –N^+ electrons with spin up of one component and N^- electrons with spin down of other component. In general, the exchange of electrons from one component to the other is continuously taking place. In the equilibrium state of the mixture, the chemical potentials of the two components of the mixture are equal. Let μ be the chemical potential of the system. We may regard these components as the fictitious system of spinless particles with the chemical potential $\mu^{\pm} = \mu \pm \mu^*B$. Then the difference of the chemical potentials of the components is

$$\mu^+ - \mu^- = (\mu + \mu^*B) - (\mu - \mu^*B) = 2\mu^*B \tag{8.12.4}$$

Let ϵ_F be the Fermi energy of the electron. At absolute zero of temperature, all the single-particle states up to the Fermi level ϵ_F are completely filled with one particle in each state, while all the single-particle states beyond ϵ_F are empty. The corresponding Fermi levels for the electrons with spin up and spin down are

$$\epsilon_F^{\pm} = \epsilon_F \pm \mu^*B \tag{8.12.5}$$

where the '+' and '-' signs stand for the spin up and spin down, respectively.

For the spinless particles, g = 1. With the help of Eq.(8.2.4), the number of particles in the two components will be

$$N^+ = 2\pi V (2m/h^2)^{3/2} F_{3/2}(z^+) \tag{8.12.6}$$

$$N^- = 2\pi V (2m/h^2)^{3/2} F_{3/2}(z^-) \tag{8.12.7}$$

where

$$F_{3/2}(z^{\pm}) = \int_0^{\infty} \epsilon^{1/2} d\epsilon \,/\, (\exp[(\epsilon - \mu^{\pm})/kT] + 1) \tag{8.12.8}$$

Then the magnetic moment per unit volume is given by

$$\langle M \rangle = 2\pi(2m/h^2)^{3/2} \mu^* [F_{3/2}(z^+) - F_{3/2}(z^-)] \tag{8.12.9}$$

We now discuss the magnetic moment at low and high temperature limits.

1. At low temperature ($kT \ll \epsilon_F$)

The Fermi energy of the electron gas (with g=2) is [see Eq.(8.2.8)]

$$\epsilon_F = (3N/4\pi gV)^{2/3} (h^2/2m) = (3\rho/4\pi g)^{2/3} (h^2/2m) \tag{8.12.10}$$

ϵ_F in this case is high because the density ρ is high and mass m of an electron is very small. At low temperatures, the free electron gas is highly degenerate.

When $z^{\pm}$ is large ($z^{\pm}>1$), $F_{3/2}(z^{\pm})$ appearing in Eq.(8.12.8) can be evaluated to give [see Eq.(8.2.18)]

$$F_{3/2}(z^+) = (2/3)(\mu^+)^{3/2} [1 + (\pi^2/8)(KT/\mu^+)^2 + (7\pi^4/640)(KT/\mu^+)^4 + \ldots] \tag{8.12.11}$$

$$F_{3/2}(z^-) = (2/3)(\mu^-)^{3/2} [1 + (\pi^2/8)(KT/\mu^-)^2 + (7\pi^4/640)(KT/\mu^-)^4 + \ldots] \tag{8.12.12}$$

Using the relations

$$\mu^{+} = \mu + \mu^{*}B$$

$$\mu^{-} = \mu - \mu^{*}B \tag{8.12.13}$$

we get

$$F_{3/2}(z^{+}) - F_{3/2}(z^{-}) = 2\mu^{*}B\mu^{1/2}\,[1 - (\pi^2/24)(KT/\mu)^2 - (35\pi^4/1920)(KT/\mu)^4 + \ldots] \tag{8.12.14}$$

where μ is the chemical potential of a free electron, which can be expressed in terms of the Fermi energy ϵ_F through Eq.(8.2.20), i.e

$$\mu = \epsilon_F\,[1 - (\pi^2/12)(KT/\epsilon_F)^2 - (\pi^4/80)(KT/\epsilon_F)^4 + \ldots] \tag{8.12.15}$$

Substituting this value in (8.12.14)

$$F_{3/2}(z^{+}) - F_{3/2}(z^{-}) = 2\mu^{*}B\epsilon_F^{1/2}[1 - (\pi^2/12)(KT/\epsilon_F)^2 - (11\pi^4/360)(KT/\epsilon_F)^4 + \ldots] \tag{8.12.16}$$

Then the low-temperature expression for the magnetic moment per unit volume is

$$\langle M\rangle = (3\rho\mu^{*2}B/2\epsilon_F)\,[1 - (\pi^2/12)(KT/\epsilon_F)^2 - (11\pi^4/360)(KT/\epsilon_F)^4 + \ldots]$$

Using the relation

$$\chi_T = \partial\langle M\rangle/\partial B \tag{8.12.17}$$

we obtain low-temperature expression for the magnetic susceptibility

$$\chi_T = (3\rho\mu^{*2}/2\epsilon_F)\,[1 - (\pi^2/12)(KT/\epsilon_F)^2 - (11\pi^4/360)(KT/\epsilon_F)^4 + \ldots] \tag{8.12.18}$$

which leads to

$$\chi_0 = 3\rho\mu^{*2}/2\epsilon_F \tag{8.12.19}$$

The the final result for low temperature ($0<T<\epsilon_F/k$) is

$$\chi_T = \chi_0\,[1 - (\pi^2/12)(KT/\epsilon_F)^2 - (11\pi^4/360)(KT/\epsilon_F)^4 + \ldots] \tag{8.12.20}$$

2. At high temperature ($kT \gg \epsilon_F$)

At high temperatures, where $z^{\pm}=\epsilon^{\mu^{\pm}/kT}$ is small, the function $F_{3/2}(z^{\pm})$ can be written as [see Eq.(8.1.7)]

$$F_{3/2}(z^{+}) = (1/2)\,\pi^{1/2}(kT)^{3/2}\,f_{3/2}(z^{+}) \tag{8.12.21}$$

$$F_{3/2}(z^{-}) = (1/2)\,\pi^{1/2}(kT)^{3/2}\,f_{3/2}(z^{-}) \tag{8.12.22}$$

where $F_{3/2}(z^{\pm})$ is given by (8.1.12). When $z^{\pm}$ is small, it is evaluated to give

$$f_{3/2}(z^{\pm}) = z^{\pm} - (1/2^{3/2})\,(z^{\pm})^2 + (1/3^{3/2})\,(z^{\pm})^3 - \ldots \quad (8.12.23)$$

Using the relations

$$z^{+} = e^{(\mu+\mu^*B)/kT} \qquad z[1 + \mu^*B/kT]$$

$$z^{-} = e^{(\mu-\mu^*B)/kT} \qquad z[1 - \mu^*B/kT] \quad (8.12.24)$$

We get

$$F_{3/2}(z^{+}) - F_{3/2}(z^{-}) = \pi^{1/2}(kT)^{3/2}\,(\mu^*B/kT)\,f_{1/2}(z) \quad (8.12.25)$$

where

$$f_{1/2}(z) = z - (1/2^{1/2})z^2 + (1/3^{1/2})z^3 - \ldots \quad (8.12.26)$$

However, it is easy to show that

$$f_{1/2}(z)/f_{3/2}(z) = 1 - (1/2^{3/2})\,f_{3/2}(z) + ((2/3^{3/2}) - (1/2^2))\,f^2_{3/2}(z) \quad (8.12.27)$$

From(8.1.13) and (8.12.10), we obtain an expression for $f_{3/2}(z)$ as

$$f_{3/2}(z) = (\rho\lambda^3/g) = (4/3\pi^{1/2})\,(\epsilon_F/kT)^{3/2} \quad (8.12.28)$$

Substituting (8.12.25) and (8.12.27) in (8.12.28), we obtain an expression for the magnetic moment per unit volume at high temperature

$$\langle M\rangle = (\rho\mu^{*2}B/kT)\,[1-(1/2^{5/2})(\rho\lambda^3)+(1/2)((1/3^{3/2})-(1/2^3))(\rho\lambda^3)^2+\ldots] \quad (8.12.29)$$

and the magnetic susceptibility at high temperature

$$\chi_T = (\rho\mu^{*2}/kT)\,[1-(1/2^{5/2})(\rho\lambda^3)+(1/2)((1/3^{3/2})-(1/2^3))(\rho\lambda^3)^2+\ldots] \quad (8.12.30)$$

When $T \to \infty$, (8.12.30) reduces to

$$\chi_\infty = \rho\mu^{*2}/kT \quad (8.12.31)$$

Finally, the high temperature expansion for the magnetic susceptibility is

$$\chi_T = \chi_\infty\,[1-(1/2^{5/2})(\rho\lambda^3)+(1/2)((1/3^{3/2})-(1/2^3))(\rho\lambda^3)^2+\ldots]$$

$$= \chi_\infty[1-(2^{1/2}/3\pi^{1/2})(\epsilon_F/kT)^{3/2}) + (16/9\pi)((2/3^{3/2})-(1/2^2))\,(\epsilon_F/kT)^3+\ldots] \quad (8.12.32)$$

Thus, the correction terms vanish as $T \to \infty$.

The variation of magnetic susceptibility per unit volume, χ_T with temperature kT/ϵ_F is shown in Fig.8.12.

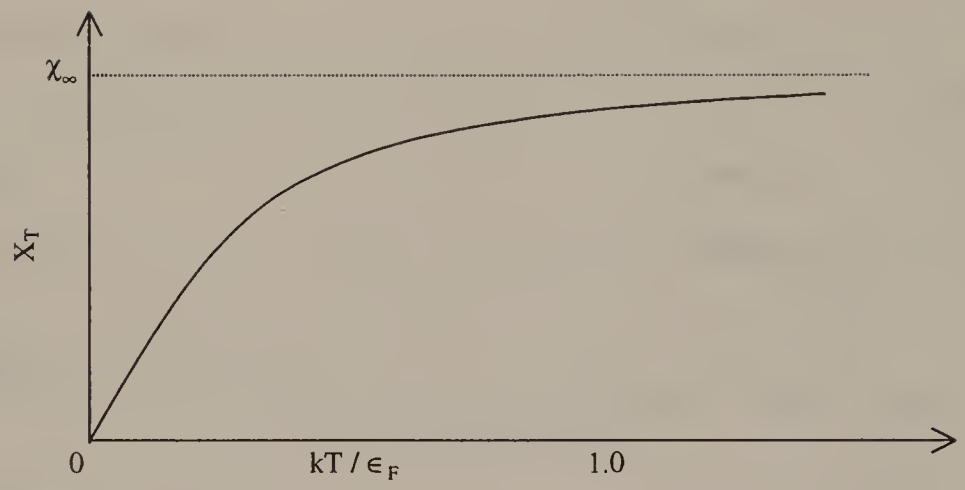


Fig.8.12. The variation of the magnetic susceptibility per unit volume χ_T with temperature kT/ϵ_F.

8.13. Landau Diamagnetism

Landau developed a theory for diamagnetism which arises from the quantisation of the orbital motion of charged particles in the presence of a magnetic field. The magnetic properties of a substance are mainly due to the electrons in the substance. In the presence of an external magnetic field, these electrons move in quantised orbits which give rise to diamagnetism.

We consider a system of N spinless electrons in the presence of an external magnetic field **B**. The Hamiltonian of a single electron is

$$H = (1/2m)\,(p + (e/v)A)^2 \qquad (8.13.1)$$

where m is the mass, (-e) is the charge of an electron and A is the vector potential related to the uniform magnetic field **B** by

$$\mathbf{B} = \nabla \times \mathbf{A} \qquad (8.13.2)$$

Let us suppose that an electron is describing a circular orbit of radius a normal to **B**, as shown in Fig.8.13.

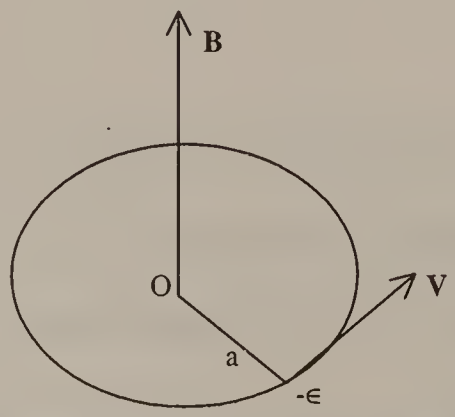


Fig.8.13. Charged particle moving in a uniform magnetic field.

The velocity **V** is tangential to the circle, which is given by

$$\mathbf{V} = \nabla_p H = (1/m)(\mathbf{P} + (e/c)\mathbf{A})$$

or

$$\mathbf{P} = m\mathbf{V} - \mathbf{A}(e/c) \tag{8.13.3}$$

According to the old quantum theory, the allowed orbits of a charged particle in an external magnetic field satisfy the quantum condition

$$\oint \mathbf{P}.d\mathbf{r} = (j + (1/2))h \quad (j = 0, 1, 2, \ldots) \tag{8.13.4}$$

Using (8.13.3), we have

$$\oint (m\mathbf{V} - (e/c)\mathbf{A}).d\mathbf{r} = (j + (1/2))h \tag{8.13.5}$$

where the line integral extends over one revolution of the orbit along the direction of motion of the electron. Changing the line integral into the surface integral and using Eq.(8.13.5), we get

$$\oint \mathbf{A}.d\mathbf{r} = \iint \nabla x\mathbf{A}.\mathbf{n}dS = \int \mathbf{B}.\mathbf{n}dS = \pi a^2 B$$

Then Eq.(8.13.5) becomes

$$2\pi amv - \pi a^2(eB/c) = (j + (1/2))h \tag{8.13.6}$$

But

$$v = (eB/mc)a$$

Thus according to the quantum condition, the radii of the allowed orbits are given by

$$a^2 = (2c/eB)(j + (1/2))\hbar \tag{8.13.7}$$

The energy corresponding to the jth allowed orbit is

$$(1/2m)(\mathbf{P} + (e/c)A)^2 = (1/2)\, mv^2 = (e\hbar/mc)B\,(j+(1/2)) \tag{8.13.8}$$

The kinetic energy associated with the linear motion along the direction of **B** is $p_z^2/2m$. Thus, the total energy of an electron is

$$\epsilon(p_z,j) = (p_z^2/2m)+(e\hbar/mc)B\,(j+(1/2)) \quad (j=0,1,2,\ldots) \tag{8.13.9}$$

Let us now calculate the degeneracy of the energy $\epsilon(p_z,j)$. When Eq.(8.13.9) is compared with that for an electron in the absence of a magnetic field, $(e\hbar/mc)B\,(j+(1/2))$ corresponds to

$$(1/2m)(p_x^2 + p_y^2)$$

and is equispaced, the energy interval between two levels is $(e\hbar/mc)B$, which is independent of the value of momentum P_B.

Corresponding to this, energy interval is defined by

$$p_B^2/2m = (e\hbar/mc)B$$

Then for a fixed value of p_z, the number of quantum states for this energy interval is given by

$$g = (2\pi V^{2/3}/h^3) \int_0^{P_B} pdp = (\pi V^{2/3}/h^3) P_B^3 = (V^{2/3}eB/hc) \qquad (8.13.10)$$

Thus the presence of a magnetic field **B** causes a g-fold degeneracy of the energy level, as shown in Fig.8.14.

The grand partition function of the system is

$$\Xi = \Pi(1 + ze^{-\beta\epsilon})$$

or

$$\ln \Xi = \sum_{\epsilon} \ln(1 + ze^{-\beta\epsilon}) \qquad (8.13.11)$$

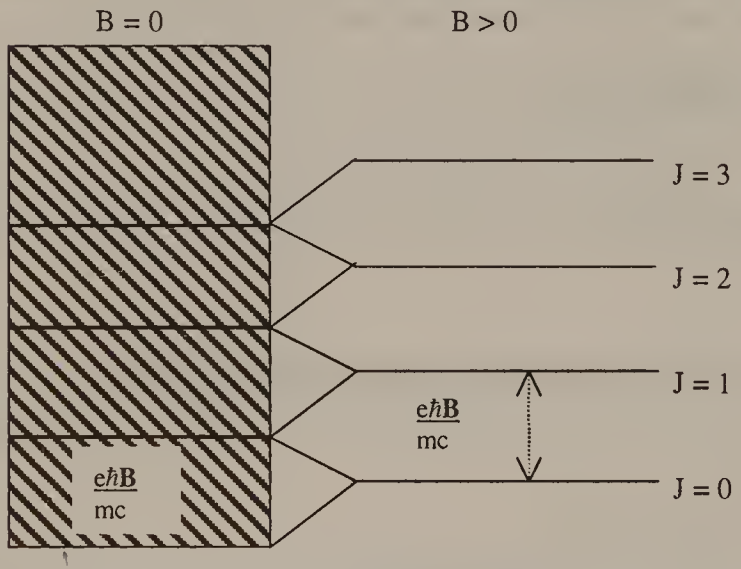


Fig.8.14. The single particle energy levels of a charged particle with an external magnetic field (B>0) and without magnetic field (B=0)

where summation is extended over all single-particle states of the system. Substituting Eq.(8.13.9) in Eq.(8.13.11) and replacing the summation over p_z by an integration, we get

$$\ln \Xi = (VeB/h^2c) \int_{-\infty}^{\infty} dp_z \sum_{j=0}^{\infty} \ln [1 + z \exp(-\beta e\hbar B(j + (1/2))/mc) \exp(-\beta P_z^2/2m)] \qquad (8.13.12)$$

Once $\ln \Xi$ is known, the average number N and the magnetic moment M of the electron gas are given by

$$N = (z(\partial/\partial z) \ln \Xi)_{B,V,T} \qquad (8.13.13)$$

and

$$M = \langle -(\partial H/\partial B) \rangle = kT\,(\partial/\partial B)\,(\ln \Xi/V)_{z,V,T} \tag{8.13.14}$$

At high temperature $z \ll 1$, and (8.13.12) is reduced to

$$\ln \Xi = (zVB/h^2c) \int_{-\infty}^{\infty} dp_z \exp(-\beta P_z^2/2m) \sum_{j=0}^{\infty} \exp(-\beta e\hbar B(j + (1/2))/mc)$$

$$= (zVeB/h^2c)\,(2\pi m/\beta)^{1/2}\,[2 \sinh(-\beta e\hbar B/2mc)]^{-1} \tag{8.13.15}$$

Then we obtain

$$N = (zV/\lambda^3)\,(a/\sinh a) \tag{8.13.16}$$

$$\langle M \rangle = (z\mu/\lambda^3)\,[(1/\sinh a) - (\cosh a/\sinh^2 a)] \tag{8.13.17}$$

where

$$a = (\beta e\hbar B/2mc) = \beta\mu B \tag{8.13.18}$$

$$\mu = e\hbar/2mc \tag{8.13.19}$$

$$\lambda = (h^2\beta/2\pi m)^{1/2} \tag{8.13.20}$$

Here μ is the Bohr magneton and λ the thermal wavelength of the particles.

From (8.13.16) and (8.13.17), we get

$$\langle M \rangle = -\rho\mu L(a) \tag{8.13.21}$$

where L(a) is the Langevin function given by Eq.(6.17.11), viz.

$$L(a) = \coth(a) - (1/a) \tag{8.13.22}$$

Substituting (8.13.21) in (8.12.17), we obtain an expression for the magnetic susceptibility per unit volume of the system.

$$\chi_T = -(\rho\mu^2/kT)\,[(1/a^2) - \operatorname{cosech}^2 a] \tag{8.13.23}$$

This result is very similar to one obtained in the Langevin theory for paramagnetism which has been discussed in Sec.6.17. The presence of the negative sign indicates that it is diamagnetic in character.

For weak magnetic field B and/or at high temperature T, such that $\mu B \ll kT$, (8.13.23) can be expanded as

$$\chi_T = -(\rho\mu^2/3kT)\,[1 - (1/12)(\mu B/kT)^2 + \ldots] \tag{8.13.24}$$

When $(\mu B/kT) \to 0$, (8.13.24) reduces to

$$\chi_T = -(\rho\mu^2/3kT) = -(C/T) \tag{8.13.25}$$

which is Curie's Law for diamagnetic substances. The Curie constant C is

$$C = (1/3)(\rho\mu^2/k) = (1/3)(\rho/k)(e\hbar/2mc)^2 \qquad (8.13.26)$$

where $(e\hbar/2mc)$ is the magnetic moment of the smallest allowed orbit. This is a direct consequence of the quantization of orbit and vanishes when $\hbar \to 0$.

Problems

8.1 Derive the distribution law according to Fermi-Dirac statistics, and with its help discuss the various properties of an ideal Fermi gas at high temperature.

8.2 Obtain an expression for the Fermi momentum of a degenerate Fermi gas at absolute zero of temperature.

8.3 Show that the kinetic energy per particle of a Fermi gas at a absolute zero is
$E_{kin} = (3/5)\epsilon_F$
where ϵ_F is the Fermi energy.

8.4 Find the energy of the highest level occupied at temperature T = 0 K for a Fermi gas. What is its value for the conduction electrons of density 1 kg/m^2.

8.5 Find an expression for the number of quantum states of an electron between energy range ϵ and $\epsilon+d\epsilon$. Show that an electron gas has finite energy at absolute zero, and obtain an expression for the average energy of an electron at this temperature.

8.6 Derive an expression for the total energy of a degenerate Fermi gas at the temperature T. Hence calculate the specific heat of the Fermi gas.

8.7 Show that the specific heat of a degenerate Fermi gas varies as
$C_v = aT + bT^3$
Obtain the values of a and b.

8.8 Show that the entropy of a degenerate Fermi gas vanishes at absolute zero of temperature whereas the pressure remains finite.

8.9 Show that for the ideal Fermi gas of N particles, the Helmholtz free energy at low temperatures is given by
$A = (3/5)N\epsilon_F[1 - (5\pi^2/12)(kT/\epsilon_F)^2 + (\pi^4/48)(kT/\epsilon_F)^4 + \ldots]$

8.10 Obtain an expression for the specific heat of a free electron gas. Indicate how it explains the specific heat of metal at low temperature.

8.11 Derive Fermi-Dirac statistics, when the number of particles of the system is not constant.

8.12 Show that the thermionic current I is given by
$I = AT^2 \exp[-b/T]$
where A and b are constants. Determine these constants.

8.13 Derive Richardson's formula for emission of electrons from a metals, when electrons are assumed to obey Fermi-Dirac statistics.

8.14 Derive an expression for photoelectric current. How it can be used to calculate the threshold frequency.

8.15 Obtain an expression for the Fermi momentum of a degenerate relativistic electron gas at absolute zero of temperature. What conclusions can be drawn from this expression regarding the stability of stars ?

8.16 An ideal free nucleon gas is enclosed in a box of volume V. The energy of a single nucleon of momentum **P** is
$\epsilon_P = (p^2/2m) + mc^2$
Assuming that there is no conservation law for the number of nucleons, calculate the partition function of the nucleon gas at temperature T and also calculate the mean energy density.

8.17 Calculate the equation of state of a completely degenerate relativistic electron gas; the energy and momentum of the electron are related by
$\epsilon = \sqrt{(c^2p^2+m^2c^4)}$

8.18 Obtain an expression for the number of states of a Fermi gas in two-dimension between the energy range E and E+dE. Derive an expression for the average energy of a two-dimensional Fermi gas at absolute zero of temperature.

8.19 Obtain an expression for the specific heat of a Fermi gas in two-dimension at finite temperature. Indicate how it differs from that of the Fermi gas in three dimension.

8.20 Discuss the Pauli theory of paramagentism of an ideal Fermi gas with intrinsic magnetic moment μ^* and spin $J\hbar$ (J = 1/2, 3/2, ...). Derive expressions for the magnetic susceptibilities of the gas at low and high temperature.

8.21 Show that paramagnetic susceptibility χ_T of a free electron gas satisfies the relation $\partial\chi_T/\partial T \to 0$ at $T \to 0$.

8.22 Show that the paramagnetic susceptibility χ_T of a free electron gas is independent of temperature T when $T \ll \epsilon_F$.

8.23 Consider a two-dimensional electron gas in a magnetic field. Taking spin paramagnetism into account, calculate the magnetic susceptibility at absolute zero.

8.24 Discuss the Landau theory of diamagnetism of an ideal Fermi gas. Derive an expression for the magnetic susceptibility of the gas at high temperature.

CHAPTER 9

CLASSICAL STATISTICAL MECHANICS OF INTERACTING SYSTEM

In the previous chapters, we have considered the (classical) ideal gases of noninteracting particles for which the equation of state is given by

$$PV/NkT = 1$$

This is valid when the gas is very rarefied and particles are far apart from one another, so that the effect of interaction is negligible. For real systems, deviations from the ideal gas law were observed experimentally and interpreted by taking the interaction between the particles of the system into consideration.

Many attempts were made to obtain an empirical equation of state which would give good agreement with the experimental results. One important relation is the virial equation of state, which is generally expressed as

$$PV/NkT = 1 + (B(T)/V) + (C(T)/V^2) + (D(T)/V^3) + \ldots$$

where the coefficients B(T), C(T), D(T) ... are called the second, third, fourth, ... virial coefficients.

Deviations from the ideal state were first interpreted qualitatively by van der Waals (1873) in terms of intermolecular interaction, which led to the famous equation of state. However, the quantitative interpretation can be given in terms of the virial coefficients, which can be expressed in terms of intermolecular interaction. At low densities, the deviations from the ideal state are adequately explained by the second virial coefficient, but at higher densities, higher virial coefficients must be taken into account.

In this chapter, we are dealing with the classical fluids with spherical symmetric molecules.

9.1. Deviations of Imperfect Gases from the Ideal State: van der Waals Equation of State

We consider a classical monatomic gas of N identical particles, each of mass m, in a container of volume V at a temperature T. The Hamiltonian of the system is given by

$$H = \sum_{i=1}^{N} (p_i^2/2m) + \Phi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \qquad (9.1.1)$$

where the function Φ is the total potential energy of the system which is dependent upon the total configuration $\{\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N\}$, and this is quite unknown. A simplification is obtained by assuming the

total potential energy as a pairwise additive, i.e.

$$\Phi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \sum_{1\le i<j\le N} u(\mathbf{r}_i, \mathbf{r}_j) \tag{9.1.2}$$

where $u(\mathbf{r}_i, \mathbf{r}_j)$ is the pair potential between particles i and j. The canonical partition function for an interacting system is defined as [see Eq.(4.8.4)]

$$Q_N = Z_N/N!\lambda^{3N} \tag{9.1.3}$$

where λ is the thermal wavelength and Z_N is the configuration integral

$$Z_N = \int \ldots \int \exp\left[-\beta \sum_{i<j} u(\mathbf{r}_i, \mathbf{r}_j)\right] \prod_{i=1}^{N} d\mathbf{r}_i$$

$$= \int \ldots \int \prod_{i<j} \{\exp[-\beta u(\mathbf{r}_i, \mathbf{r}_j)]\} \prod_{i=1}^{N} d\mathbf{r}_i \tag{9.1.4}$$

The exact evaluation of Z_N is technically impossible- at least at present. However, we simplify the analysis when the interaction between particles is very small. In such a case, the Boltzmann factor, $e^{-\beta\Phi}$ can be approximated as

$$e^{-\beta\Phi} = \prod_{i<j} \exp[-\beta u(\mathbf{r}_i, \mathbf{r}_j)] = 1 + (N(N-1)/2)f_{12} + \ldots \tag{9.1.5}$$

where

$$f_{12} \equiv f(\mathbf{r}_1, \mathbf{r}_2) = \exp[-\beta u(\mathbf{r}_1, \mathbf{r}_2)] - 1 \tag{9.1.6}$$

Then the partition function can be written as

$$Q_N = Q_N^{id}\,[1 + (1/2)\,(N(N-1)/V^2) \int f_{12}\, d\mathbf{r}_1\, d\mathbf{r}_2 + \ldots] \tag{9.1.7}$$

where Q_N^{id} is the partition function for the ideal gas and given by Eq.(4.8.7). Since N is large, one can neglect '1' in comparison to N. Using the relation

$$A = -kT \ln Q_N \tag{9.1.8}$$

the Helhmholtz free energy of the imperfect gas is given by

$$A = A^{id} - (1/2)\,(N^2kT/V^2) \int f_{12}\, d\mathbf{r}_1\, d\mathbf{r}_2 \tag{9.1.9}$$

where A^{id} is the free energy of an ideal gas

$$A^{id} = NkT\,[\ln\rho - 1 - 3\ln\lambda] \tag{9.1.10}$$

$u(\mathbf{r}_1, \mathbf{r}_2)$ is a function of the interatomic separation $r = |\mathbf{r}_1 - \mathbf{r}_2|$ between two atoms and hence f_{12} is also a function of r only. Using the Jacobi transformation

$$d\mathbf{r}_1\, d\mathbf{r}_2 = d\mathbf{r}_1\, d\mathbf{r}$$

where

$$\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$$

Equation (9.1.9) can be written as

$$A = A^{id} + (NkT/V)\, B(T) \qquad (9.1.11)$$

where

$$B(T) = -(1/2)\, N \int f(r)\, d\mathbf{r} = -(1/2)\, N \int (e^{-\beta u(r)} - 1)\, d\mathbf{r} \qquad (9.1.12)$$

Then, the equation of state is given by

$$(PV/NkT) = 1 + (1/V)\, B(T) \qquad (9.1.13)$$

where $p^{id} = NkT/V$

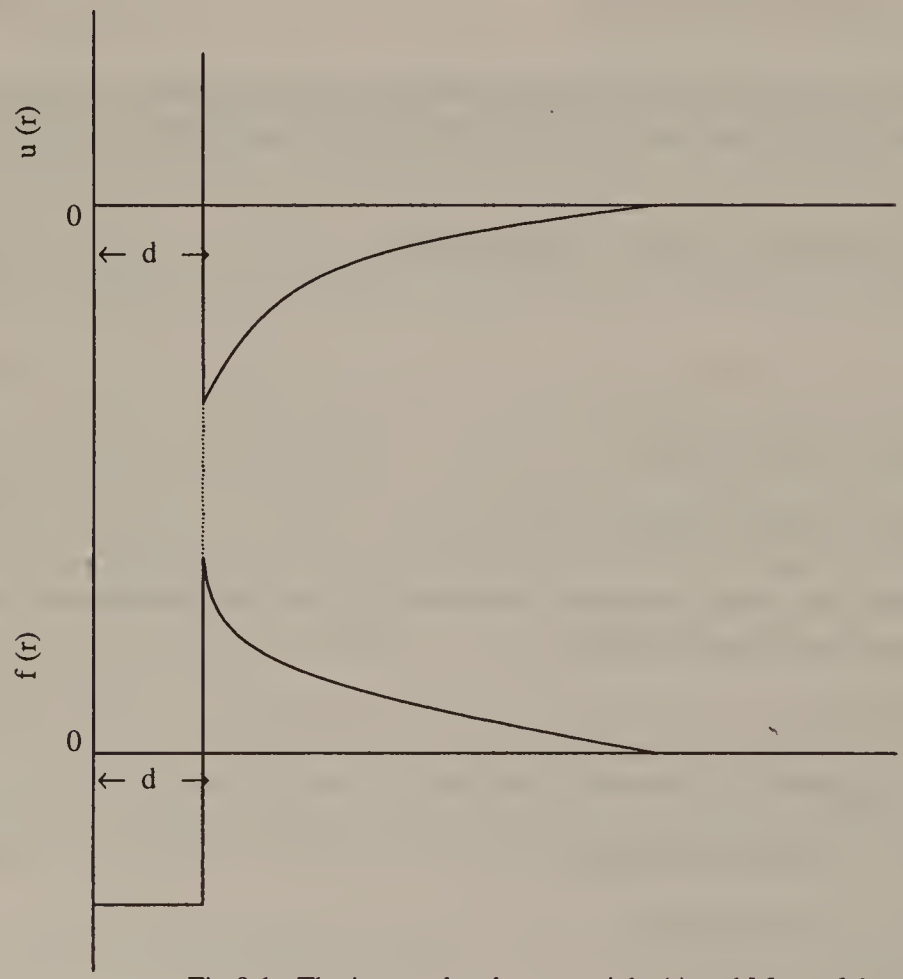


Fig.9.1. The intermolecular potential u(r) and Mayer f-function

Evaluation of B(T) depends on the nature of pair potential. In order to derive the equation of state, van der Waals (1973) made the simplifying assumption that the molecules are rigid spheres of

diameter d and attract each other with a weak force, which rapidly decreases as the distance increases, i.e.

$$u(r) = \infty \qquad r < d$$

$$= \phi^{o}(r) \qquad r > d \tag{9.1.14}$$

A typical plot of the function u(r) and f(r) is shown in Fig.9.1. We see that the function f(r) becomes negligibly small as r becomes large in comparison to the effective range of potential u(r). Thus, the function corresponding to the pair potential (9.1.14) is

$$f(r) = 1 \qquad r < d$$

$$\phi^{o}(r)/kT \qquad r > d \tag{9.1.15}$$

Substituting (9.1.15) in (9.1.12) and dividing the limit of integration into the repulsive and attractive regions, we get

$$B(T) = [b - (a/NkT)] / N \tag{9.1.16}$$

where

$$b = 2\pi N \int_{0}^{d} r^2 \, dr = 2\pi N d^3/3 \tag{9.1.17a}$$

$$a = -2\pi N^2 \int_{d}^{\infty} \phi^{o}(r) \, r^2 \, dr \tag{9.1.17b}$$

b is a function of the hard-sphere diameter, while a depends on the nature of the attractive part of pair potential.

Substituting this value in (9.1.11), we obtain an expression for the free energy of the gas

$$A = A^{id} + (NkT/V) [b - (a/NkT)] \tag{9.1.18}$$

Since V is large in comparision to b, i.e. $b/V << 1$, then using the relation

$$\ln [1 - (b/V)] = -b/V$$

(9.1.18) can be written as

$$A = A^{id} - NkT \ln (1 - b/V) - (a/V) \tag{9.1.19}$$

From this it is clear that when V is large, it reduces to the expression for the free energy of an ideal gas, but V cannot be less than b, since the argument of the logarithm becomes negative when $V < b$.

From (9.1.13), the pressure of the gas is expressed as

$$P = (NkT/V) [1 + (b/V)] - (a/V^2) = (NkT/(V - b)) - (a/V^2) \tag{9.1.20a}$$

or

$$(P + (a/v^2)) (V - b) = NkT \tag{9.1.20b}$$

Equation (9.1.20b) is the famous van der Waals equation of state, which is theoretically correct up to terms in 1/V. This equation has been applied empirically to study the real gases over a wide range of densities and temperature. We demonstrate some isotherms corresponding to van der Waals equation of state in Fig.9.2. The van der Waals curves give maxima and minima in the region represented by a horizontal line in the experimental curve (not shown in the figure). These maxima and minima points come closer with the rise in temperature. There exists a temperature T_c, called the critical temperature, at which the kink (i.e. maxima and minima) in the isotherm disappears. The point of inflection C is called the critical point. It is only below $T < T_c$ that the van der Waals equation of state gives a kink in an isotherm. For a given P and $T < T_c$, P has generally three roots in V (e.g., the values V_1, V_2 and V_3 shown in Fig.9.2).

The critical point for the van der Waals gas can be determined from Eq.(9.1.20a) by imposing the conditions

$$(\partial P/\partial V)_T = -(NkT/(V-b)^2) + (2a/V^3) = 0 \qquad (9.1.21a)$$

$$(\partial^2 P/\partial V^2)_T = (2NkT/(V-b)^3) + (6a/V^4) = 0 \qquad (9.1.21b)$$

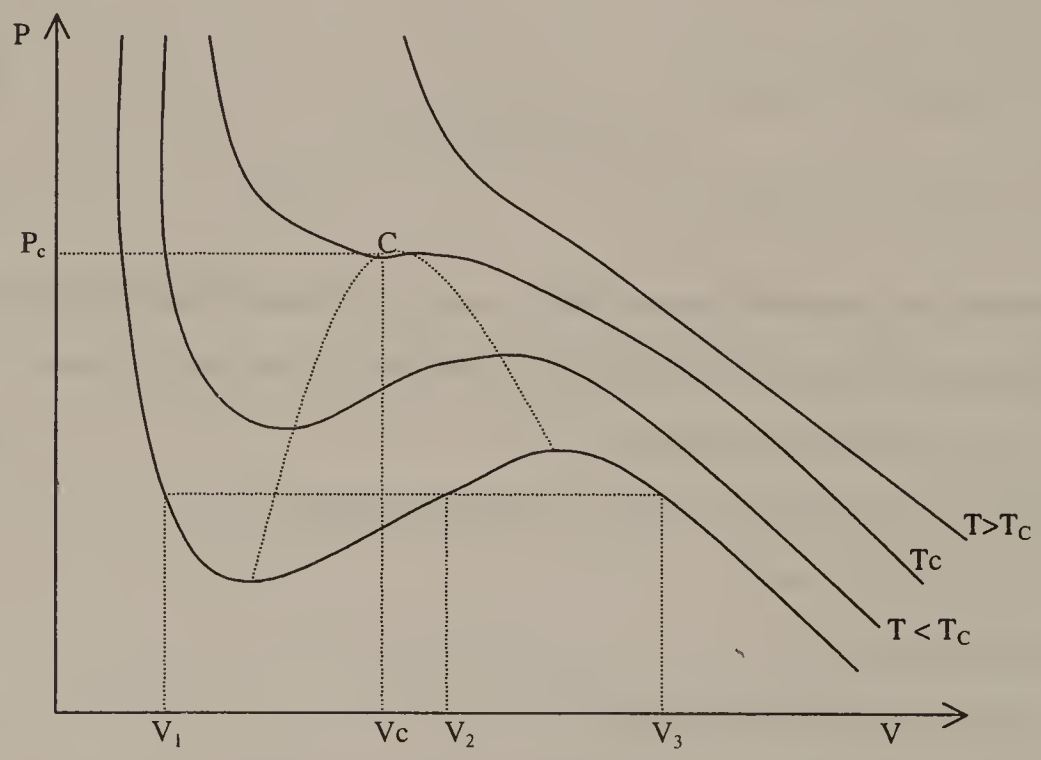


Fig.9.2. PV diagram of the van der Waals equation of state

Equations (9.1.20) and (9.1.21) can be solved to give

$$V_c = 3b$$

$$T_c = 8a/27bNk$$

$$P_c = a/27b^2 \tag{9.1.22}$$

where V_c, T_c and P_c are, respectively, known as the critical volume, critical temperature and critical pressure.

When the pressure, temperature and volume are measured in units of P_c, T_c and V_c respectively, then the van der Waals equation of state (9.1.20b) becomes

$$(P_r + (3/V_r^2))(V_r - (1/3)) = (8/3)T_r \tag{9.1.23}$$

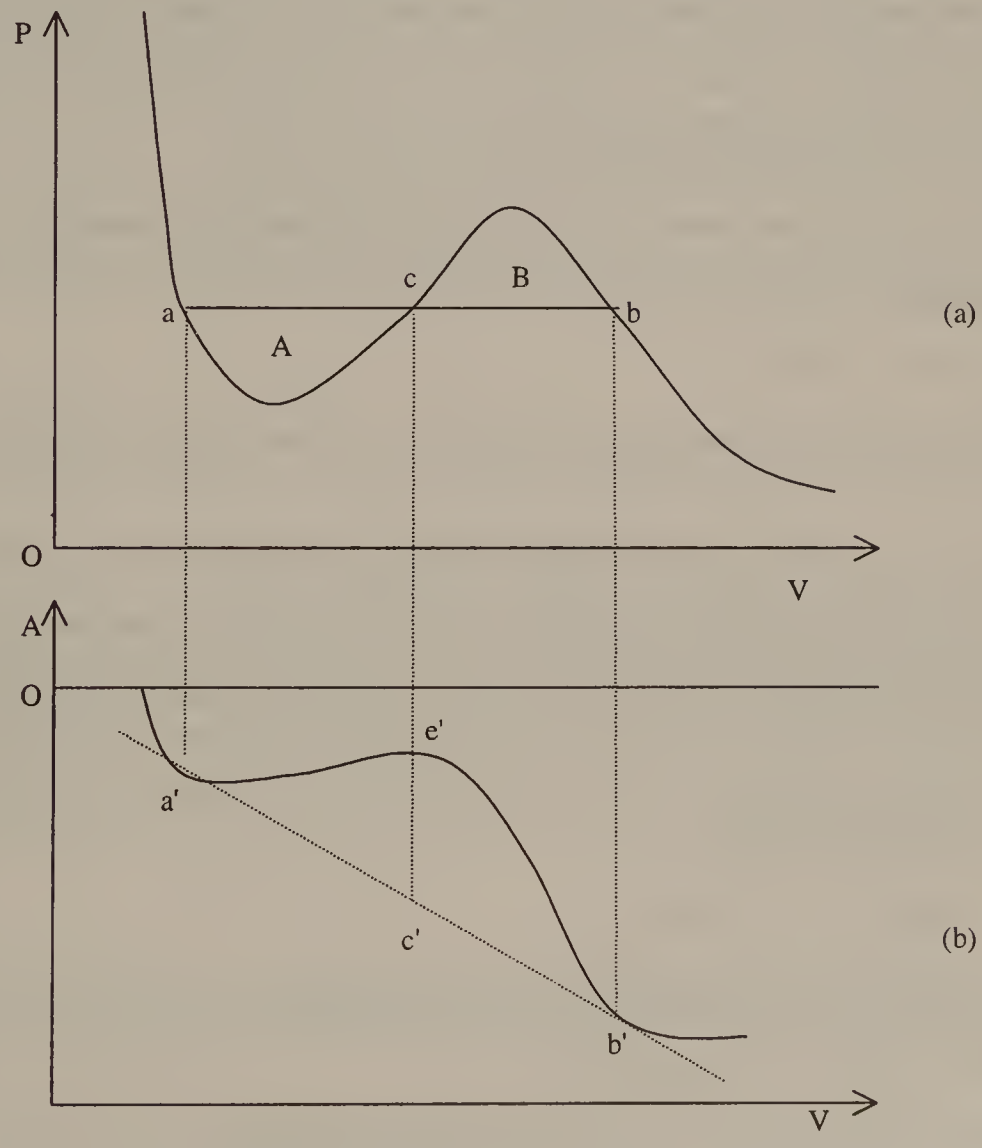


Fig.9.3. The Maxwell construction for a van der Waals isotherm

where

$$P_r = P/P_c$$

$$T_r = T/T_c$$

$$V_r = V/V_c \qquad (9.1.24)$$

Here P_r, T_r and V_r are, respectively, called the reduced pressure, reduced temperature and reduced volume. Equation (9.1.23) does not contain any constant characteristic of gas and hence, it is a universal equation valid for all substance. This is called the law of corresponding states.

The discrepancy between the theoretical and the experimental curves for $T<T_c$ can be explained on the basis of the instability of equilibrium. When $T < T_c$, there is an unphysical region where $\partial P/\partial V > 0$. Thus, the isotherms at $T < T_c$ violate the stability condition, since according to statistical mechanics, $\partial P/\partial V \leq 0$ is the stability condition. In order to remove this difficulty, Maxwell (1974) proposed the equal area construction (i.e.(area) A = (area) B, for the van der Waals isotherm) by drawing a horizontal line in this region as shown in Fig.9.3(a).

This geometrical construction is known as the Maxwell construction.

We now describe a method of drawing the horizontal line according to the Maxwell construction and eliminate the unphysical portions of the van der Waals isotherm by this procedure. Let us first describe the Maxwell construction. In terms of pressure, the free energy A(T,V) at fixed temperature T may be defined as

$$A(T, V) = -\int P\, dV \qquad (9.1.25)$$

which is the area under an isotherm in a P-V diagram. This is reported in Fig.9.3(b) showing a kink in the free energy A. However, for the equilibrium situation it should be minimal.

For the A-V curve [Fig.9.3(b)], there is one common tangent line a'c'b'; the points a' and b' are the corresponding common tangent points. Since $P = -(\partial A/\partial V)_T$, the tangent line a'c'b' [of Fig.9.3(b)] corresponds to the horizontal line abc of [Fig.9.3(a)]. Any point c' on the tangent line lies lower than the point e' on the van der Waals free energy curve at the same T and V and hence, corresponds to the equilibrium situation. Thus, the horizontal line acb in the P-V diagram which has the same P and T values, represents the mixture of two phases. In other words, the system undergoes a first order phase transition.

Let us interpret the Maxwell construction as follows. The condition of common pressure at points a and b in the P–V diagram gives

$$-(\partial A/\partial V)_{V=V_a} = -(\partial A/\partial V)_{V=V_b} \qquad (9.1.26)$$

while the condition of the common tangent line in the A-V diagram is

$$((A_b - A_a)/(V_b - V_a)) = (\partial A/\partial V)_{V=V_a} \qquad (9.1.27)$$

With the help of Eqs.(9.1.25) and (9.1.26, 9.1.27) we obtain the final result

$$P_a(V_b - V_a) = -(A_b - A_a) = \int_{V_a}^{V_b} P\, dV \qquad (9.1.28)$$

where P_a is the pressure at the point a in the P-V diagram. This clearly shows that (area) A = (area) B of Fig.9.3(a).

Since the states a and b have the same P and T values, they can be interpreted as the pure liquid and pure-vapour end points respectively, of a liquid-vapour transition lines. The wiggles in the van der Waals curves explain the metastable state, i.e. super-cooled and super-saturated states. These states are observed experimentally. However, there is no satisfactory theory to explain these states.

The van der Waals equation of state and Maxwell construction are the first step to explain the deviation from the ideal behaviour and are still important at present from the heuristic point of view.

9.2. Cluster Expansion for Classical Systems

The cluster expansion of the classical partition function is an important tool for most of our theoretical understanding of the equilibrium properties of fluids. It was developed principally by Mayer and his colleagues in terms of Mayer f-function and is directly applicable to dilute imperfect gases. However, it has been generalized in a variety of ways.

We start with the expression (9.1.3) for the canonical partition function, where Z_N is the configuration integral. We introduce the Mayer function f_{ij} defined by the relationship

$$f_{ij} = f(r_{ij}) = \exp[-\beta u(\mathbf{r}_i, \mathbf{r}_j)] - 1 \tag{9.2.1}$$

where $u(\mathbf{r}_i, \mathbf{r}_j)$ is the pair potential between molcules i and j. Then the Boltzmann factor W_N is written as

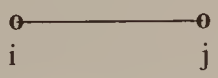
$$W_N(\mathbf{r}_i, \mathbf{r}_j, \ldots, \mathbf{r}_N) \equiv \exp[-\beta\Phi] = \prod_{1\le i<j\le N} [1 + f_{ij}] \tag{9.2.2}$$

or, in expanded form, we have

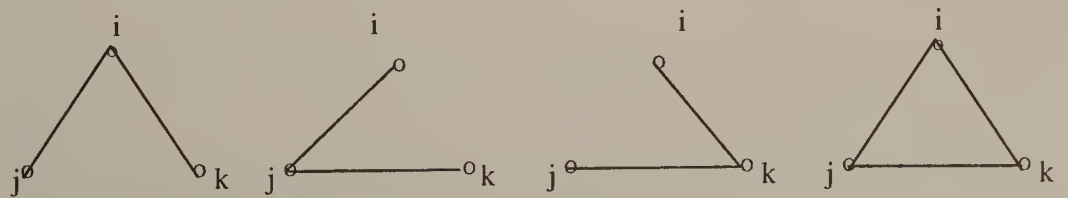
$$W_N(\mathbf{r}_i, \mathbf{r}_j, \ldots, \mathbf{r}_N) = 1 + \sum_{i<j} f_{ij} + \sum_{i<j}\sum_{k<l} f_{ij}f_{kl} + \sum_{i<j}\sum_{k<l}\sum_{m<n} f_{ij}f_{kl}f_{mn} + \ldots \tag{9.2.3}$$

By introducing the Mayer f-function, the effect of intermolecular forces is more clearly exposed, since the function f_{ij} becomes zero for large r_{ij}, the contribution of each term becomes zero if the argument $r_{ij} = |\, r_i - r_j \,|$ of a function in the term is large.

In terms of the Mayer f-function, we form a cluster which is a collection of points (molecules) connected directly or indirectly by the f-function. For instance, a cluster of two particles is



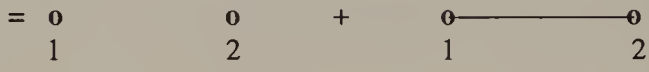
In general, there are many ways in which any given set of particles may be connected together to form a cluster. For example, a cluster of three particles i, j and k may be formed in any of the four ways.



Ursell (1927) devised an alternative method of expansion of Boltzmann factor W_N in terms the U-function. Thus

$$W_1(\mathbf{r}_1) = U_1(\mathbf{r}_1) = 1 = o_1 \tag{9.2.4a}$$

$$W_2(\mathbf{r}_1, \mathbf{r}_2) = U_1(\mathbf{r}_1)\, U_1(\mathbf{r}_2) + U_2(\mathbf{r}_1, \mathbf{r}_2)$$



(9.2.4b)

$$W_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = U_1(\mathbf{r}_1)\, U_1(\mathbf{r}_2)\, U_1(\mathbf{r}_3) + U_2(\mathbf{r}_1, \mathbf{r}_2)\, U_1(\mathbf{r}_3) + U_2(\mathbf{r}_1, \mathbf{r}_3)\, U_1(\mathbf{r}_2) + U_2(\mathbf{r}_2, \mathbf{r}_3)\, U_1(\mathbf{r}_1)$$

$$+ U_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \tag{9.2.4c}$$

$$W_N(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = U_1(\mathbf{r}_1) \ldots U_1(\mathbf{r}_N) + \ldots + U_N(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \tag{9.2.4d}$$

or

$$W_N(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = 1 + \sum_{i<j} U_2(\mathbf{r}_i, \mathbf{r}_j) + \sum_{i<j<k} U_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) + \ldots + U_N(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \tag{9.2.5}$$

U_N is the contribution due to all N particles closed to one another. $U_N(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \sim 0$ unless the particles are "clustered". Solution of these equations in terms of U-functions yields

$$U_1(\mathbf{r}_1) = W_1(1) \tag{9.2.6a}$$

$$U_2(\mathbf{r}_1, \mathbf{r}_2) = W_2(\mathbf{r}_1, \mathbf{r}_2) - W_1(\mathbf{r}_1)\, W_2(\mathbf{r}_2) \tag{9.2.6b}$$

$$U_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = W_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) - W_2(\mathbf{r}_1, \mathbf{r}_2)\, W_1(\mathbf{r}_3) - W_2(\mathbf{r}_1, \mathbf{r}_3)\, W_1(\mathbf{r}_2) - W_2(\mathbf{r}_2, \mathbf{r}_3)\, W_1(\mathbf{r}_1)$$

$$+ 2W_1(\mathbf{r}_1)\, W_1(\mathbf{r}_2)\, W_1(\mathbf{r}_3) \tag{9.2.6c}$$

and so on. The U_l are called Ursell cluster functions or more briefly, Ursell functions. The Ursell function method is more general; and is not based on the assumption of additivity of the pair potential. Further, this method can be extended to include the quantum mechanical system.

On comparing Eqs.(9.2.3) and (9.2.5) we find that the U_l functions may be given explicitly by the relation

$$U_l(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_l) = \sum_{(C_l)} \prod_{C_l} f_{ij} \tag{9.2.7}$$

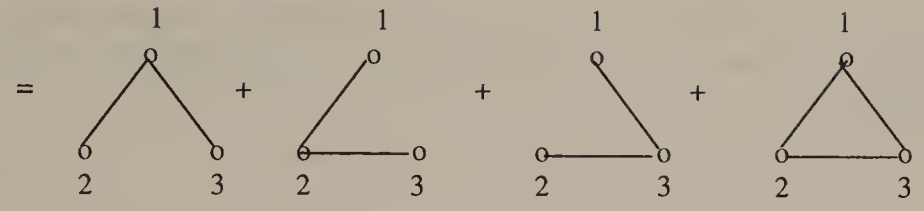
where the sum of the products is carried out over all connected diagrams with l labelled points C_l. For example, the first four Ursell functions are given by

$$U_1(\mathbf{r}_1) = 1 \tag{9.2.8a}$$

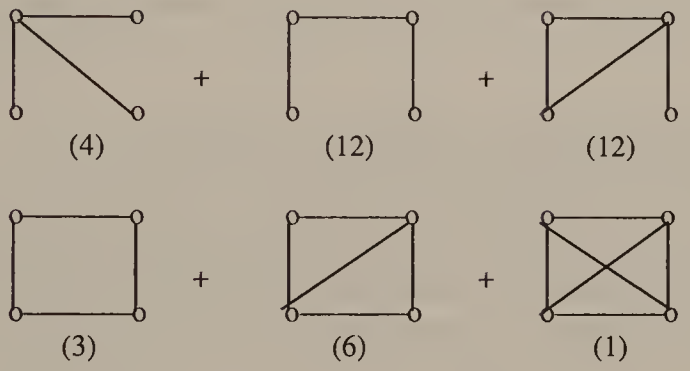
$$U_2(\mathbf{r}_1, \mathbf{r}_2) = f_{12} =$$

(9.2.8b)

$$U_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = f_{12} f_{13} + f_{12} f_{23} + f_{13} f_{23} + f_{12} f_{13} f_{23}$$



(9.2.8c)



$U_4(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_4) =$

(9.2.8d)

The expression for U_4 has 38 terms, the number of terms belonging to each types is shown in the brackets ( ). Since the W_l possesses the product property, it follows from the above equations that the U_l possesses the cluster properties. We now define the cluster integral b_l by

$$b_l(V,T) = (1/l!V) \int \ldots \int U_l(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_l) \prod_{i=1}^{l} d\mathbf{r}_i \tag{9.2.9}$$

where the limits of integrations correspond to the physical dimensions of the container of volume V. The first few cluster integrals are

$$b_1 = (1/V) \int d\mathbf{r}_1 = 1 \tag{9.2.10a}$$

$$b_2 = (1/2!V) \int U_2(\mathbf{r}_1, \mathbf{r}_2)\, d\mathbf{r}_1\, d\mathbf{r}_2 = (1/2) \int f_{12}\, d\mathbf{r}_{12} \tag{9.2.10b}$$

$$\begin{aligned} b_3 &= (1/3!V) \int U_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)\, d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3 \\ &= (1/6V) \int [f_{12}f_{13} + f_{12}f_{23} + f_{13}f_{23} + f_{12}f_{13}f_{23}]\, d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3 \\ &= (1/2) \int f_{12}f_{13}\, d\mathbf{r}_{12}\, d\mathbf{r}_{13} + (1/6) \int f_{12}f_{13}f_{23}\, d\mathbf{r}_{12}\, d\mathbf{r}_{13} \\ &= 2b_2^2 + (1/6) \int f_{12}f_{13}\, f_{23}\, d\mathbf{r}_{12}\, d\mathbf{r}_{13} \end{aligned} \tag{9.2.10c}$$

$$b_4 = (1/4!V) \int U_4(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4)\, d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3\, d\mathbf{r}_4 \tag{9.2.10d}$$

and so on.

We can now express the configurational integral Z_N in terms of the cluster integral b_l. The product of the U's represents a set of m_l cluster ($l = 1, 2, \ldots$) for specified molecules.

We consider a system of N particles. Let it consist of a number of cluster which represents m_1 unit clusters, m_2 clusters of two molecules ..., m_l cluster of l molecules, then total number of molecules is governed by the condition

$$\sum_{i=1}^{N} l m_l = N \tag{9.2.11}$$

and a product of the U's, representing such a number of clusters, yields an integral over $d\mathbf{r}_1\, d\mathbf{r}_2 \ldots d\mathbf{r}_N$ of

$$I = (1!Vb_1)^{m_1} (2!Vb_2)^{m_2} \ldots (l!Vb_l)^{m_l} \ldots = \prod_{l=1}^{N} (l!Vb_l)^{m_l} \tag{9.2.12}$$

Let us find out the number of different ways in which N molecules can be divided into clusters. Since the indistinguishability of the molecules has already been taken into consideration by the factor $(N!)^{-1}$ in Eq.(9.1.3), the N molecules can be regarded as distinguishable. However, the molecules with a cluster as well as the cluster of the same size are taken to be indistinguishable, leading to identical terms. The number of ways in which N distinguishable molecules are distributed among the labelled boxes so that there are one molecule in each of m_1 boxes, two molecules in each of m_2 boxes ..., l molecules in each of m_l boxes is given by

$$N!/(1!)^{m_1} (2!)^{m_2} \ldots (l!)^{m_l} = N!/\prod_{l=1}^{N} (l!)^{m_l} \tag{9.2.13}$$

However, there is exchange of all molecules of one cluster with all the molecules of another cluster of the same size. The number of such exchanges among clusters with l molecules is $m_l!$. So the total number of distinct ways in which N molecules can be distributed into m_l clusters of l particles is obtained by dividing (9.2.13) by $m_1!m_2!\ldots m_l!$.

Thus, the number of different ways of dividing N distinguishable molecules into clusters so that there are m_l cluster of l molecules is

$$N!/\prod_{l=1}^{N} (l!)^{m_l} m_l! \tag{9.2.14}$$

The product of Eqs.(9.2.12) and (9.2.14) is the contribution to Z_N. Thus, the contribution to Z_N is

$$N! \prod_{l=1}^{N} (Vb_l)^{m_l} / m_l! \tag{9.2.15}$$

We obtain the configurational integral Z_N from (9.2.15) by summing over all sets of m_l with the condition (9.2.11). Thus, we can write

$$Z_N = N! \sum_{(m_l)} \left[\prod_{l} (Vb_l)^{m_l} / m_l! \right] \tag{9.2.16}$$

and

$$Q_N = (1/\lambda^{3N}) \sum_{(m_l)} [\prod_l (Vb_l)^{m_l} / m_l!] \tag{9.2.17}$$

Next, we express the grand partition function Ξ in terms of the cluster integrals b_l. The grand partition function for a classical system is given by Eq.(5.1.16) i.e.

$$\Xi = \sum_{N=0}^{\infty} z'^N Q_N \tag{9.2.18}$$

where

$$z'^N = z'^{\sum l m_l} = \prod_l (z'^l)^{m_l} \tag{9.2.19}$$

Substituting (9.2.17) and (9.2.19) in (9.2.18) and noting that a summation over all values of N is equivalent to a summation over all possible sets $\{m_l\}$ with the conditions $\sum_l l m_l = N$, we obtain

$$\Xi = \sum_{(m_l)} [\prod_l (Vb_l/\lambda^{3l})^{m_l} (1/m_l!)] \prod_l (z'^l)^{m_l}$$

$$= \sum_{(m_l)} [\prod_l (Vb_l z'^l/\lambda^{3l})^{m_l} / m_l!]$$

$$= \sum_{(m_l)} [\prod_l (Vb_l z^l)^{m_l} / m_l!] \tag{9.2.20}$$

where $z = z'/\lambda^3$.

It can be rearranged to give .

$$\Xi = \prod_l [\sum_{(m_l)} (Vb_l z^l)^{m_l} / m_l!] = \prod_l [\exp (Vb_l z^l)] \tag{9.2.21}$$

or

$$V^{-1} \ln \Xi = \sum_{l \geq 1} b_l z^l \tag{9.2.22}$$

We use this expression of the grand partition function to obtain the expansion of pressure in powers of fugacity z. The pressure P is given by the relation

$$\beta P = \lim_{V \to \infty} V^{-1} \ln \Xi = \sum_{l \geq 1} b_l z^l \tag{9.2.23}$$

Equation (9.2.23) gives the pressure in powers of z. The number density $\rho = N/V$ is obtained from (9.2.22) as

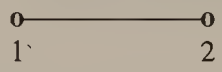
$$\rho = (1/v) = \lim_{V \to \infty} [(1/V) z (\partial \ln \Xi / \partial z)_{T,V}] = \sum_{l \geq 1} l b_l z^l \tag{9.2.24}$$

Equations (9.2.23) and (9.2.24) are the famous cluster expansions of the Mayer-Ursell formalism.

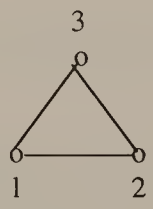
Husami (1950) has simplified the problem by introducing another function V_k, defined by the equation

$$V_k(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_k) = \Sigma \Pi f_{ij} \tag{9.2.25}$$

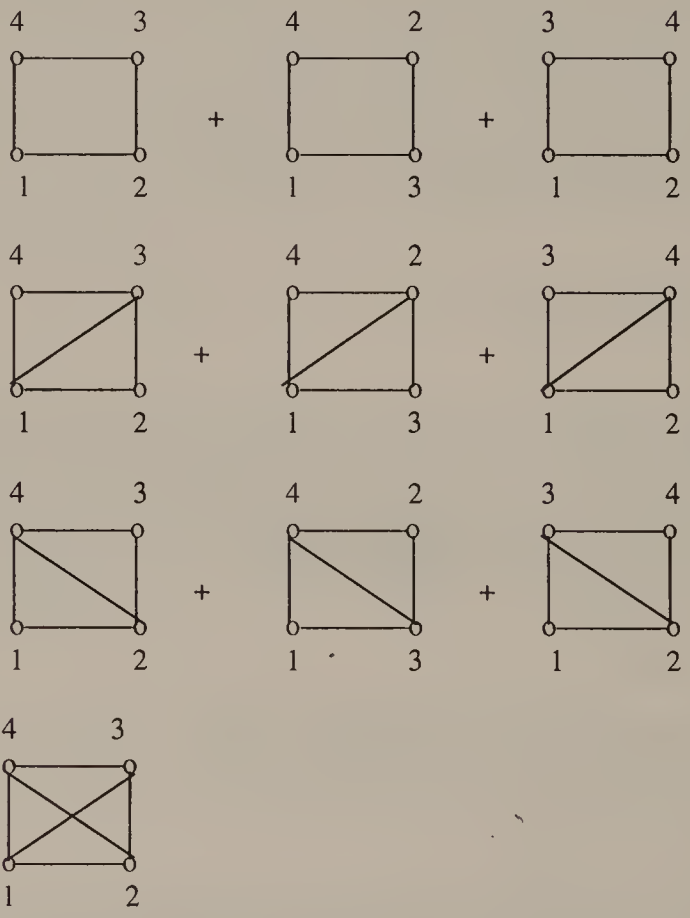
where the sum of the product is carried out over all stars, which can be formed from k lebelled points. The V-function is called star function or Husami function. The simple Husami functions are

$V_2(\mathbf{r}_1, \mathbf{r}_2) = f_{12} =$ 

(9.2.26a)

$V_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) =$ 

(9.2.26b)

$V_4(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) =$ 

(9.2.26c)

It can be easily seen that the Ursell function U_i can be expanded in terms of the Husami functions V_k. Thus,

$$U_2(\mathbf{r}_1, \mathbf{r}_2) = V_2(\mathbf{r}_1, \mathbf{r}_2) \tag{9.2.27a}$$

$$U_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = V_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) + V_2(\mathbf{r}_1, \mathbf{r}_2)\, V_2(\mathbf{r}_1, \mathbf{r}_3) + V_2(\mathbf{r}_1, \mathbf{r}_2)\, V_2(\mathbf{r}_2, \mathbf{r}_3) + V_2(\mathbf{r}_1, \mathbf{r}_3)\, V_2(\mathbf{r}_2, \mathbf{r}_3) \tag{9.2.27b}$$

$$U_4(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) = V_4(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) + \sum_{(12)} V_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)\, V_2(\mathbf{r}_3, \mathbf{r}_4)$$

$$+ \sum_{(12)} V_2(\mathbf{r}_1, \mathbf{r}_2)\, V_2(\mathbf{r}_2, \mathbf{r}_3)\, V_2(\mathbf{r}_3, \mathbf{r}_4) + \sum_{4} V_2(\mathbf{r}_1, \mathbf{r}_2)\, V_2(\mathbf{r}_1, \mathbf{r}_3)\, V_2(\mathbf{r}_1, \mathbf{r}_4) \tag{9.2.27c}$$

and so on. The number of terms belonging to each sum is shown in the bracket.

We now define the irreducible cluster integral by the relation

$$\beta_k = (1/k!V) \int \ldots \int V_{k+1}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_{k+1}) \prod_{i=1}^{k+1} d\mathbf{r}_i \tag{9.2.28}$$

k is called the index of the irreducible cluster. It is found that an irreducible cluster with index k contains k + 1 molecules. From (9.2.28), the first few irreducible cluster integrals are

$$\beta_1 = (1/V) \int V_2(\mathbf{r}_1, \mathbf{r}_2)\, d\mathbf{r}_1\, d\mathbf{r}_2 = \int V_2(\mathbf{r}_1, \mathbf{r}_2)\, d\mathbf{r}_2 \tag{9.2.29a}$$

$$\beta_2 = (1/2V) \int V_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)\, d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3$$

$$= (1/2) \int V_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)\, d\mathbf{r}_2\, d\mathbf{r}_3 \tag{9.2.29b}$$

$$\beta_3 = (1/6V) \int V_4(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4)\, d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3\, d\mathbf{r}_4 \tag{9.2.29c}$$

Finally, we derive a relationship between the b_l's and the β_l's. Substituting (9.2.27) in (9.2.10) and using (9.2.29), we can express b_2, b_3 and b_4 in terms of β_4

$$b_2 = (1/2) \left[\int V_2(\mathbf{r}_1, \mathbf{r}_2)\, d\mathbf{r}_2 \right] = (1/2)\, \beta_1 \tag{9.2.30a}$$

$$b_3 = (1/3!V) \int [V_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) + 3V_2(\mathbf{r}_1, \mathbf{r}_2) V(\mathbf{r}_1, \mathbf{r}_3)] d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3$$

$$= (1/3) \left[(1/2) \int V_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)\, d\mathbf{r}_2\, d\mathbf{r}_3 \right] + (1/2) \left[\left(\int V_2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 \right) \left(V_2(\mathbf{r}_1, \mathbf{r}_3)\, d\mathbf{r}_3 \right) \right]$$

$$= (1/3)\beta_2 + (1/2)\, \beta_1^2 \tag{9.2.30b}$$

$$b_4 = (1/4!) \int [V_4(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) + 12V_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)\, V_2(\mathbf{r}_1, \mathbf{r}_4) + 12V_2(\mathbf{r}_1, \mathbf{r}_2)\, V_2(\mathbf{r}_2, \mathbf{r}_3)\, V_2(\mathbf{r}_3, \mathbf{r}_4)$$

$$+ 4V_2(\mathbf{r}_1, \mathbf{r}_2)\, V_2(\mathbf{r}_1, \mathbf{r}_3)\, V_2(\mathbf{r}_1, \mathbf{r}_4)] d\mathbf{r}_1 d\mathbf{r}_3 d\mathbf{r}_4$$

$$= (1/4)\beta_3 + \beta_1\beta_2 + (2/3)\, \beta_1^3 \tag{9.2.30c}$$

and so on.

In general every cluster integral b_l can be expressed in terms of the irreducible cluster integrals β_k. Let us consider a cluster integral b_l, which contains β_k irreducible clusters of index k (k = 1, 2, ..., l-1). Then, the contribution to b_l of a product of the V's is

$$(1/l!) \prod_{k=1}^{l-1} (k!\, \beta_k)^{n_k} \tag{9.2.31}$$

The number of ways in which l distinguishable molecules are distributed into n_1 sets of 2, ..., n_k sets of k + 1 doubly connected molecules is

$$(l!/l^2) \prod_{k=1}^{l-1} (l/k!)^{n_k} (1/n_k!) \tag{9.2.32}$$

The product of (9.2.27) and (9.2.32) is

$$(1/l^2) \prod_{k=1}^{l-1} (l\beta_k)^{n_k}/n_k! \tag{9.2.33}$$

which is the contribution to b_l of all the products of V's corresponding to a given set of numbers n_1, n_2, ..., n_k. Since the number of V's with k indices is n_k, the total number of different indices (molecules) is

$$l = \prod_{k=1}^{l-1} kn_k + 1 \tag{9.2.34}$$

Then we can express the cluster integral b_l in terms of the irreducible cluster integral β_k as

$$b_l = (1/l^2) \sum_{nk} \prod_{k=1}^{l-1} (l\beta_k)^{n_k}/n_k! \tag{9.2.35}$$

where the summation is over all non-specified sets of n_k, which satisfies the condition (9.2.34). From (9.2.35), one can reproduce values of b_l's given by (9.2.30).

9.3. Virial Expansion of the Equation of State

In this section, we obtain the expression of the equation of state in the form

$$\beta P = \sum_{l=1}^{\infty} B_l \rho^l \tag{9.3.1}$$

which is known as the virial expansion of the equation of state and B_l is called the lth virial coefficient. Equation (9.3.1) can be obtained by eliminating the fugacity z between (9.2.21) and (9.2.22).

Equation (9.2.22) can be written as

$$z = \rho [1 + \sum_{l=2} l b_l z^{l-1}]^{-1} \tag{9.3.2}$$

Taking help of (9.3.2), it can be expanded in the form

$$z = \rho [1 - \beta_1 z - ((1/2)\beta_1^2 + \beta_2)z^2 - ((2/3)\beta_1^3 + 2\beta_1\beta_2 + \beta_3)z^3 - \dots] \tag{9.3.3}$$

This can be solved by the method of iteration. Thus,

$$z = \rho [1 - \beta_1\rho + ((1/2)\beta_1^2 - \beta_2)\rho^2 - ((1/6)\beta_1^3 - \beta_1\beta_2 + \beta_3)\rho^3 + \dots] \tag{9.3.4}$$

or in general

$$z = \rho \exp[-\sum_{l=1}^{\infty} \beta_l \rho^l] \tag{9.3.5}$$

where the β_l are the irreducible cluster integrals. Equation (9.3.5) expresses the fugacity as a function of the density ρ. Next we eliminate z from Eq.(9.2.21).

Substituting Eqs.(9.3.2) and (9.3.5) in Eq.(9.2.21), we get

$$\beta P = \rho - (1/2)\,\beta_1\,\rho^2 - (2/3)\,\beta_2\,\rho^3 - \ldots \tag{9.3.6}$$

This can also be obtained in an easy way, starting from the equation (5.3.9)

$$\beta P = \ln \Xi / V \tag{9.3.7}$$

Differentiating (9.3.7) with respect to z, we get

$$\beta(dP/dz) = (1/V\Xi)\,(d\Xi/dz) = (1/V\Xi) \sum_{N=0}^{\infty} (Nz^{N-1}/N!)Z_N = (1/Vz)\,\langle N\rangle = \rho/z,$$

where

$$\langle N\rangle = \Xi^{-1} \sum_{N=0}^{\infty} (Nz^N Z_N/N!)$$

Then,

$$\beta(dP/d\rho) = (\rho/z)\,(dz/d\rho) = \rho(d(\ln z)/d\rho)$$

or

$$\beta P = \int_0^{\rho} \rho'(d(\ln z)/d\rho')d\rho' \tag{9.3.8}$$

Substituting (9.3.5), we obtain

$$\beta P = \rho - \sum_{l=1}^{\infty} (l/(l+1))\,\beta_l\,\rho^{l+1} \tag{9.3.9}$$

Comparing Eqs.(9.3.1) and (9.3.9), the virial coefficient are defined as

$$B_1 = 1 \tag{9.3.10a}$$

$$B_l = -((l-1)/l)\,\beta_{l-1} \qquad l \geq 2 \tag{9.3.10b}$$

From (9.3.10b), the first few virial coefficient are

$$B_2 = -(1/2)\,\beta_l \tag{9.3.11a}$$

$$B_3 = -(2/3)\,\beta_2 \tag{9.3.11b}$$

Finally the second and third virial coefficient for the spherical molecules are written as

$$B_2 = -(1/2V)\int f_{12}\,d\mathbf{r}_1 d\mathbf{r}_2 = -(1/2)\int f_{12}\,d\mathbf{r}_2 \tag{9.3.12a}$$

$$B_3 = -(1/3V)\int f_{12} f_{13} f_{23}\,d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 = -(1/3)\int f_{12} f_{13} f_{23}\,d\mathbf{r}_2 d\mathbf{r}_3 \tag{9.3.12b}$$

These expressions are valid for monatomic molecules, each with three translational degree of freedom. In this case the pair interaction potential depends only on the separation of molecules.

We now consider diatomic and other linear molecules, which are represented as rigid rotators with three translational and two rotational degree of freedom. The interaction potential for such molecules may be assumed to be a function of intermolecular separation as well as orientation of the molecules. In this case the Mayer function f_{ij} is defined by the relation

$$f_{ij} \equiv f(x_i x_j) = \exp[-\beta u(x_i,x_j)] - 1 \tag{9.3.13}$$

where $u(x_i,x_j)$ is the pair potential between molecules i and j and the vector $x_i = (\mathbf{r}_i, \omega_i)$, where $\mathbf{r}_i$ is the position vector and $\omega_i \equiv (\theta_i, \phi_i)$ is the orientation of molecule i. For the linear molecules, the virial coefficients can be written as

$$B_2 = -(1/2V)\int f(x_1x_2)dx_1dx_2 \tag{9.3.14a}$$

$$B_3 = -(1/3V)\int f(x_1x_2)\,f(x_1x_3)\,f(x_2x_3)\,dx_1dx_2dx_3 \tag{9.3.14b}$$

where

$$dx_i = (1/4\pi)\,d\mathbf{r}_i\,d\omega_i = (1/4\pi)\,d\mathbf{r}_i\,\sin\theta_i\,d\theta_i\,d\phi_i \tag{9.3.15}$$

Using the transformation

$$d\mathbf{r}_1\,d\mathbf{r}_2 = d\mathbf{r}_1 d\mathbf{r}$$

$$d\phi_1\,d\phi_2 = d\phi_1 d\phi$$

where $\mathbf{r} = r_1 - \mathbf{r}_2$ and $\phi = \phi_2 - \phi_1$, we can write

$$dx_1dx_2 = (1/16\pi^2)\,d\mathbf{r}_1 d\mathbf{r}\,\sin\theta_i\,d\theta_i\,\sin\theta_2\,d\theta_2\,d\phi_1\,d\phi$$

Then (9.3.14a) can be expressed as

$$B_2 = -(1/4)\int f(r\omega_1\omega_2)\,r^2 dr\,\sin\theta_1\,d\theta_1\,\sin\theta_2\,d\theta_2\,d\phi \tag{9.3.16}$$

This equation will be used in the next section for calculation of the virial coefficient.

It has been confirmed that the contribution of higher order virial coefficients increases with density ρ. At liquid density, one has to consider several terms of the series. However, the expansion diverges at high density. Hence, this expansion approach to the equation of state is suitable at low density, where the series converges.

9.4. Intermolecular Potential Function

The prediction of the virial coefficients requires an accurate knowledge of the molecular potential function. We first consider the nature of the intermolecular forces which form the potential of different molecules.

9.4.1. Nature of intermolecular forces

The forces of interaction between molecules are attractive at large distances and repulsive at short distances. The forces between atoms or molecules is essentially electrostatic in character which is the resultant force between the electrons and nuclei of two system. This force F(r) depends only on the distance between their centres. If u(r) is the potential energy of two molecules due to the intermolecular forces F(r), then u(r) is related to F(r) by the equation

$$F(r) = -du(r)/dr$$

u(r) is often called the pair potential.

The potential energy u(r) at any value of r is sum of two energies i.e.

$$u(r) = u_A(r) + u_R(r) \tag{9.4.1}$$

where $u_A(r)$ and $u_R(r)$ are, respectively, the attractive and repulsive potential energy.

(A) Attractive energy

Let us consider two atoms bound together chemically to form a diatomic molecule. As a result, some distortion of the original electron configurations of the atoms occurs. This molecule is electrostatistically equivalent to a positive charge q = ne and a negative charge –q separated by a distance x (n being the number of protons of charge +e). The two charges may be considered to form an electric dipole of moment $\mu = qx$. Such a molecule possesses a 'permanent electric dipole' and is known as a 'polar' molecule.

There are molecules such as HCl, which possess a permanent dipole moment. When the positive and negative charges in a molecule coincide, we have non poplar molecules such as O_2 and N_2, which does not possess a permanent dipole moment. When the polar molecules approach each other, they tend to turn in such a way that the opposite charges face each other. Consequently the dipole-dipole interaction is attractive.

When molecules do not have a permanent dipole moment, they acquire it in an external elastic field **E**. In this field the two charges are displaced slightly in opposite directions so that a dipole moment $\mu_i = \alpha \mathbf{E}$ is form, where μ_i is called an induced dipole moment and α is the polarizability of the molecule.

Let us consider two non-polar molecules A and B. The electrons in these molecules are moving rapidly round the corresponding nuclei. At any instant the molecule A may have an instantaneous dipole moment, which induces a dipole in B in that instant. This gives rise to an instantaneous force of attraction between them. It is changing rapidly with time. The average value of this instantaneous attractive force over all corresponding electron configurations in the molecules gives the dispersive force.

Thus the potential energy of attraction u_A between two molecules is sum of three terms i.e.

$$u_A = u_{perm} + u_{in} + u_{dis} \tag{9.4.2}$$

where u_{perm} is the interaction between two permanent dipoles, u_{in} is the interaction of the induced dipole in one molecule with the permanent dipole of the other and u_{dis} is the dispersion energy. They are given by

$$u_{perm} = 2\mu^4/3kTr^6 \tag{9.4.3}$$

$$u_{in} = -2\alpha\mu^2/r^6 \tag{9.4.4}$$

$$u_{dis} = -\alpha^2 E_i/r^6 \tag{9.4.5}$$

where E_i is the ionization energy.

We can now write the resultant interaction energy between two molecules as

$$u_A(r) = -A/r^6 \tag{9.4.6}$$

where A is a positive quantity. u_A is known as the van der Waals interaction energy.

(B) Repulsive energy

When two molecules approach each other very closely, a strong repulsive force acts between them. This is due to the fact that a molecule occupies a certain volume in space and prevents other molecules from entering into this region. The repulsive energy is expressed in a reasonably good approximation as

$$u_R(r) = B/r^n \qquad 9 \le n \le 15 \tag{9.4.7}$$

where B is constant.

Then the resultant interaction energy is

$$u(r) = (A/r^n) - (A/r^6) \tag{9.4.8}$$

Lennard-Jones and Devonshire in 1937 suggested that n = 12.

9.4.2. Intermolecular potential models

We consider some intermolecular potential models, which are frequently used in calculating the various properties.

(i) Hard sphere model

Because of its simplicity, the hard sphere model has been extensively used in the studies of properties of the system. For a hard sphere system, the pair potential is defined as

$$\begin{aligned} u(r) &= \infty \qquad \text{for } r < d \\ &= 0 \qquad \text{for } r > d \end{aligned} \tag{9.4.9}$$

and shown in Fig.9.4a, d being the diameter of the hard sphere. hence the Mayer function f(r) is

$$\begin{aligned} f(r) &= -1 \qquad \text{for } r < d \\ &= 0 \qquad \text{for } r > d \end{aligned} \tag{9.4.10}$$

which is also demonstrated in Fig.9.4b.

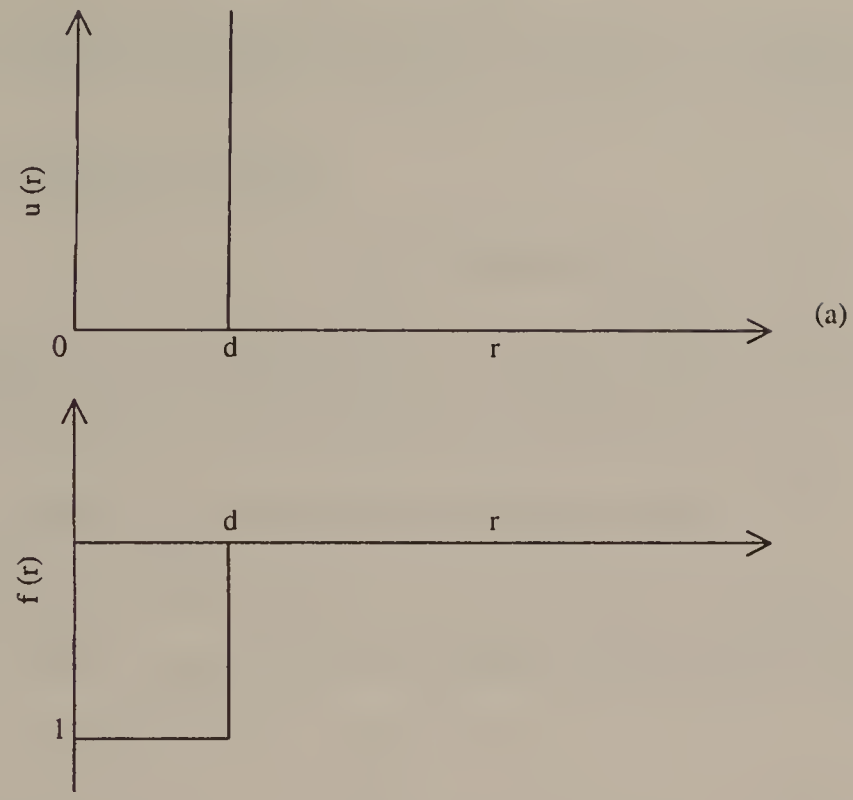


Fig.9.4. (a) The hard sphere potential u(r) and (b) hard sphere Mayer function f(r)

(ii) Lennard-Jones (12-6) potential model
The Lennard-Jones (12-6) potential is defined by

$$u(r) = 4\epsilon\,[(\sigma/r)^{12} - (\sigma/r)^{6}] \tag{9.4.11}$$

where $u(r) = 0$ at $r = \sigma$ and $u(r) = -\epsilon$ at $r_m = 2^{1/6}\sigma$ and demonstrated in Fig.9.5. It is a realistic potential for spherical non-polar molecules. It has been widely used for the calculation of the properties of fluids.

(iii) Keesom potential model
In this model, the pair potential is defined as

$$u(r, \theta_1, \theta_2, \phi_2 - \phi_1) = \infty \qquad \text{for } r < \sigma$$

$$= -(\mu^2/r^3)\, g(\theta_1, \theta_2, \phi_2\text{-}\phi_1) \qquad \text{for } r > \sigma \tag{9.4.12}$$

where

$$g(\theta_1,\theta_2,\phi_2-\phi_1) = 2\cos\theta_1 \cos\theta_2 - \sin\theta_1 \sin\theta_2 \cos(\phi_2-\phi_1) \tag{9.4.13}$$

the angles θ_1, θ_2, ϕ_1 and ϕ_2 define the relative orientations of the two dipoles as shown in Fig.9.6. This model represents hard spheres of diameter σ, which contains an embedded point dipole of strength μ. This potential model includes the short range repulsive forces and the dipole-dipole interaction.

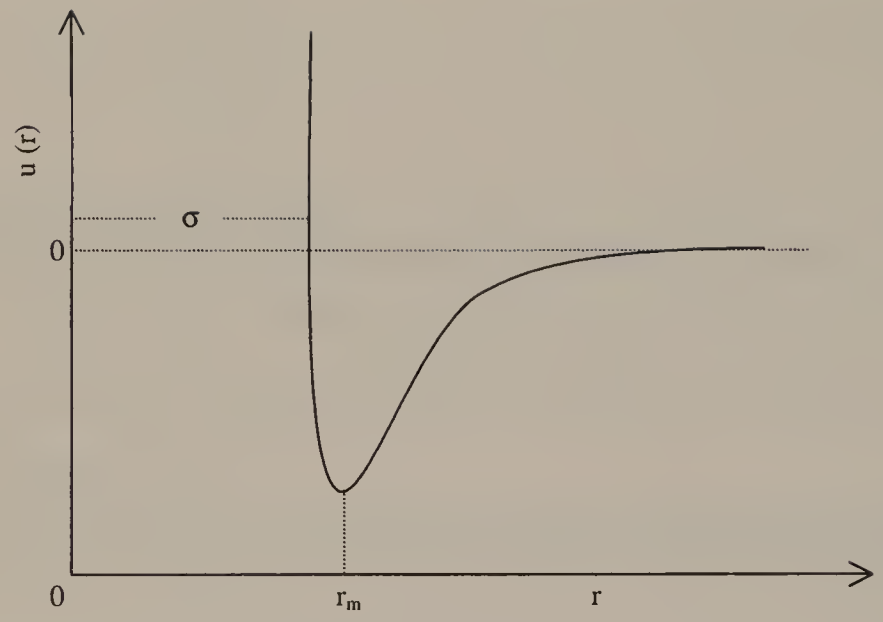


Fig.9.5. The Lennard-Jones (12-6) potential u(r) as a function of r, at σ, u(r) = 0 and $r_m = 2^{16}\sigma$, $u(r) = -\epsilon$

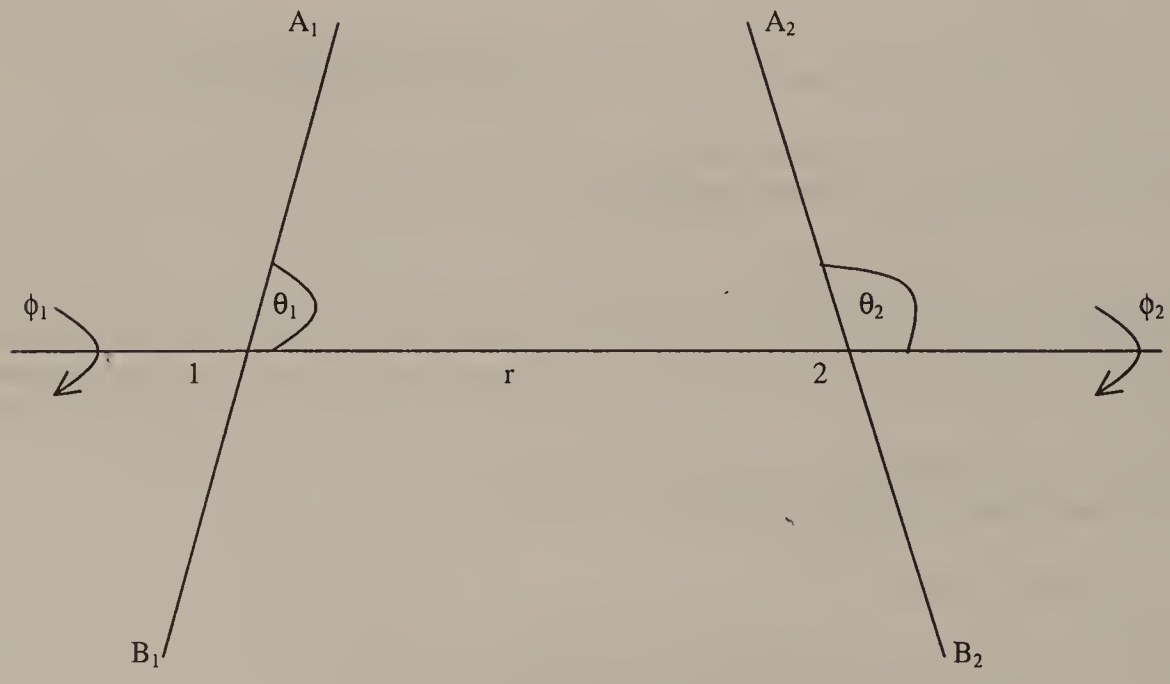


Fig.9.6. The coordinates describing the orientations of two polar molecules. Points 1 and 2 represent the centres of two molecules 1 and 2. The lines A_1B_1 and A_2B_2 indicate the axises of molecules 1 and 2. The intermolecular distance is r and angles $\theta_1,\theta_2,\phi_1,\phi_2$ define the orientation of the two molecules.

the angles θ_1, θ_2, ϕ_1 and ϕ_2 define the relative orientations of the two dipoles as shown in Fig.9.6. This model represents hard spheres of diameter σ, which contains an embedded point dipole of strength μ. This potential model includes the short range repulsive forces and the dipole-dipole interaction.

(iv) Stockmayer potential model

This potential model is defined as

$$u(r, \theta_1, \theta_2, \phi_2 - \phi_1) = 4\epsilon [(\sigma/r)^{12} - (\sigma/r)^6] - (\mu^2/r^3)\, g(\theta_1, \theta_2, \phi_2 - \phi_1) \tag{9.4.14}$$

where $g(\theta_1, \theta_2, \phi_2 - \phi_1)$ is given by (9.4.13). This potential function includes the Lennard Jones (12-6) potential and the dipole-dipole interaction. It is useful for those polar molecules for which dipole-quadrupole and higher multipole interactions are not important.

We compute the virial coefficients for these potential models in the next section.

9.5. Evaluation of Virial Coefficients of the Equation of State

(i) Hard sphere model

For a hard sphere fluid calculation of B_2 is very straight. From Eq.(9.3.11a), we find that for hard sphere model

$$B_2 = -2\pi \int_0^d (-1)\, r^2 dr = 2\pi d^3/3 \equiv b_0 \tag{9.5.1}$$

Eq.(9.3.11b) reduces to

$$B_3 = -(1/3) \int f_{12}\, a_{12}\, d\mathbf{r}_2 \tag{9.5.2}$$

where

$$a_{12} = \int f_{13}\, f_{23} d\mathbf{r}_3 \tag{9.5.3}$$

In order to evaluate this integral, we introduce bipolar coordinates (see Fig.9.7); we fix the positions of the particles 1 and 2 and let particle 3 take all possible positions. Rotation of the element of area dx dy about the x axis sweeps out $d\mathbf{r}_3$, so that

$$d\mathbf{r}_3 = 2\pi y\, dx\, dy \tag{9.5.4}$$

The coordinates x and y can be transformed to r_{13} and r_{23} by relation

$$r_{13}^2 = x^2 + y^2$$

$$r_{23}^2 = y^2 + (r_{12} - x)^2$$

Using the Jacobian transformation, we obtain

$$dx\, dy = (r_{13} r_{23}/y r_{12})\, dr_{13}\, dr_{23} \tag{9.5.5a}$$

or

$$d\mathbf{r}_3 = (2\pi r_{13} r_{23}/r_{12})\, dr_{13}\, dr_{23} \tag{9.5.5b}$$

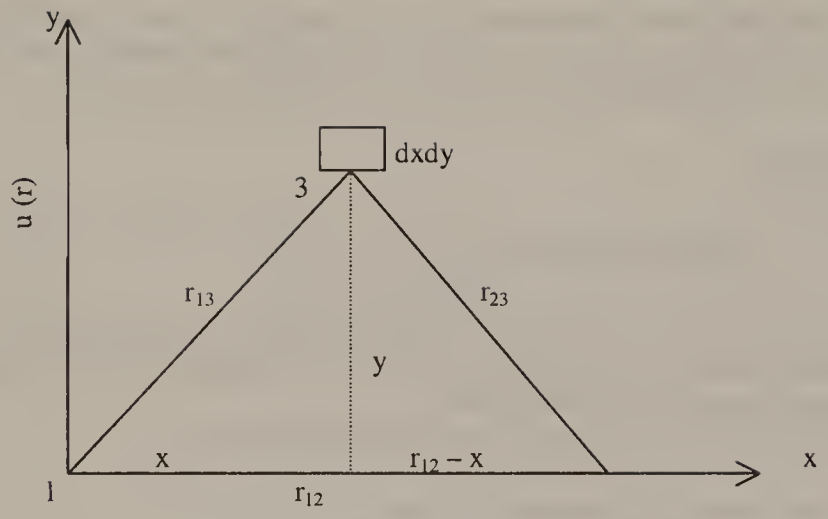


Fig. 9.7. Bipolar coordinates

In the case of hard sphere system, since $f_{ij} = -1$ for $r_{ij} < d$, a_{12} can be written as

$$a_{12} \equiv a(r_{12}) = (2\pi/r_{12}) \int_0^d r_{13}\, dr_{13} \int_0^d r_{23}\, dr_{23} \tag{9.5.6}$$

which represents the volume common to two spheres of radius d with centres separated by distance r_{12}. The only region contributing to the integral is ABC in Fig. 9.8.
Thus, we can evaluate the integral as

$$a_{12} = (2\pi/r_{12}) \int_{r_{12/2}}^{d} r_{13}\, dr_{13} \int_{|r_{12}-r_{13}|}^{r_{13}} r_{23}\, dr_{23}$$

$$= (4\pi d^3/3)\,[1 - (3/4)\,(r_{12}/d) + (1/16)(r_{12}/d)^3] \tag{9.5.7}$$

Substituting this value in (9.5.2), we finally get the result for B_3 as

$$B_3 = (16\pi^2 d^6/9) \int_0^1 [1 - (3/4)\, r_{12}^* + (1/16)\, r_{12}^{*3}]\, dr_{12}^{*2}\, dr_{12}^*$$

$$= (5\pi^2 d^6/18) = (5/8)\, b_0^2 \tag{9.5.8}$$

where $r_{12}^* = r_{12}/d$.
The fourth virial coefficient B_4 of the hard sphere gas is also known exactly (Boltzmann 1899; majumdar 1929)

$$B_4 = [-(89/280) + (219\sqrt{2}/2240\pi) + (4131/2240\pi)\tan^{-1}(\sqrt{2})]\, b_0^3$$

$$= 0.28695\, b_0^3 \tag{9.5.9}$$

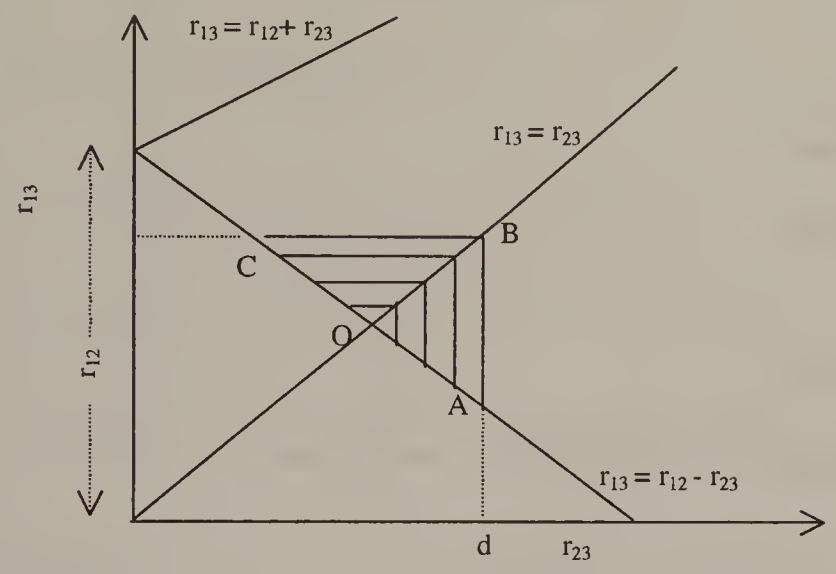


Fig.9.8. Limits of integration in Eq.(9.5.6)

The virial coefficient up to B_7 have been estimated for the hard sphere gas. However, the determination of virial coefficients B_l becomes much more complicated with increasing l. The results are listed in Table 9.1.

Table 9.1. The Reduced Virial Coefficients $B_l^* \equiv B_l/(b_0)^l$ for the hard sphere fluid.

B_2^*	1
B_3^*	5/8
B_4^*	0.28695
B_5^*	0.1103 ± 0.0003
B_6^*	0.0386 ± 0.0004
B_7^*	0.0138 ± 0.0004

The virial coefficients for hard spheres are temperature independent, and are positive. Therefore the equation of state $\beta P/\rho \equiv PV/NkT$ is a function of density only.

(ii) Lennard-Jones (12-6) potential

For calculating the second virial coefficient for the Lennard-Jones (12-6) potential, we use Eq.(9.3.11a) and integrate it by parts,

$$B_2 = -(2\pi/3kT) \int_0^\infty r^3 (\partial u(r)/\partial r) \exp(-u(r)/kT)\, dr \qquad (9.5.10)$$

In terms of the reduced quantities

$$r^* = r/\sigma$$

$$T^* = kT/\epsilon$$

the reduced second virial coefficient is

$$B_2^* = B_2/(2\pi\sigma^3/3) = B_2/b_0$$

where

$$b = 2\pi\sigma^3/3$$

Substituting (9.4.11) in (9.5.10), we get

$$B_2^*(T^*) = -(4/T^*)\int_0^\infty \exp[-(4/T^*)(r^{*-12} - r^{*-6})][-12r^{*-12} + 6r^{*-6}]\, r^{*2}dr^*$$

$$= \int_0^\infty (\partial/\partial r^*)\{\exp[-(4/T^*)(r^{*-12} - r^{*-6})]\}\, r^{*3}dr^* \qquad (9.5.11)$$

This integration may be performed analytically when $\exp.(4r^{*-6}/T^*)$ is expanded in an infinite series. Then, Eq. (9.5.11) can be given in a form which is integrable analytically. Thus,

$$B_2^*(T^*) = -(4/T^*)\int_0^\infty \exp(-(4/T^*)\, r^{*-12})[-12r^{*-12}]\, r^{*2}dr^*$$

$$-3\sum_{i=1}^\infty (1/i!)(4/T^*)^i \int_0^\infty \exp(-(4/T^*)\, r^{*-12})\, r^{*-6i}\, r^{*2}dr^* \qquad (9.5.12)$$

Putting $4r^{*-12}/T^* = x$, we can write (9.5.12) in the form

$$B_2^*(T^*) = (4/T^*)^{1/4}\int_0^\infty e^{-x}x^{-1/4}dx - (1/4)\sum_{i=1}^\infty (1/i!)(4/T^*)^{(2i+1)/4}\int_0^\infty e^{-x}x^{(2i-5)/4}dx$$

$$= (4/T^*)^{1/4}\,\Gamma(3/4) - \sum_{i=1}^\infty (1/4i!)(4/T^*)^{(2i+1)/4}\,\Gamma((2i-1)/4) \qquad (9.5.13)$$

where $\Gamma(y)$ is the gamma function. Then, the final result can be given by

$$B_2^*(T^*) = T^{*-1/4}\sum_{i=0}^\infty b_i T^{*-i/2} \qquad (9.5.14)$$

where the coefficient b_i is given is given by

$$b_i = -(2^{i+1/2}/4i!)\,\Gamma((2i-1)/4) \qquad (9.5.15)$$

Evaluating the first few coefficients b_i, the reduced second virial coefficient B_2^* is expressed as

$$B_2^* = T^{*-1/4}[1.733 - 2.564T^{*-1/2} - 8.66T^{*-1} - 4.27T^{*-3/2} - \ldots] \quad (9.5.16)$$

This series converges rapidly for $T^* \geq 4$.

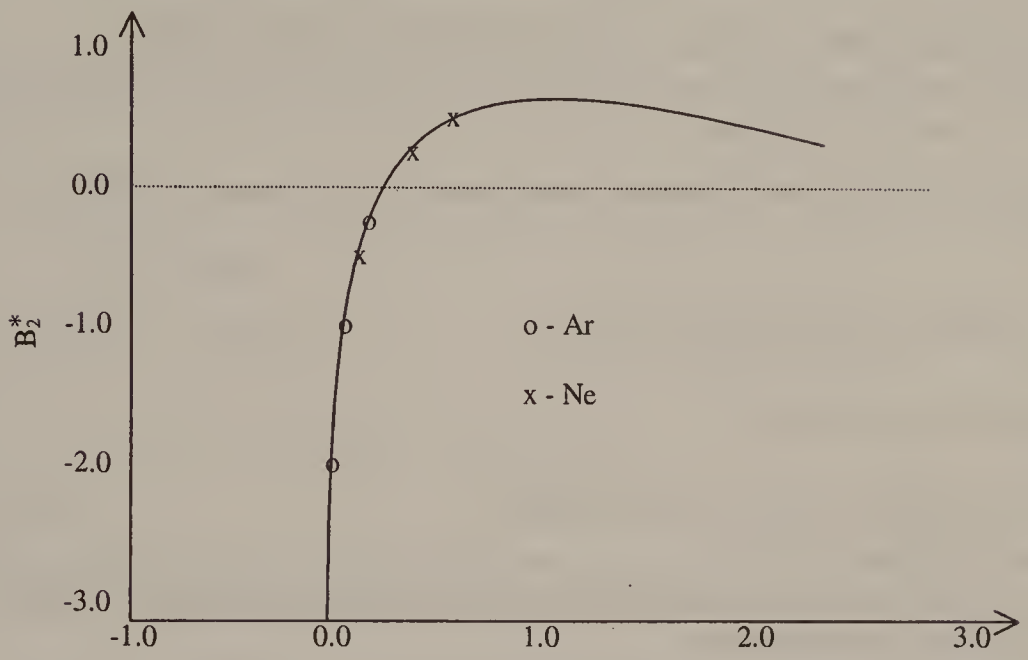


Fig.9.9. The reduced second virial coefficient B_2^* for the Lennard-Jones (12-6) fluid as a function of temperature T^*

We find that B_2^* is a function of T^* only. The values of B_2^* are plotted as a function of T^* in Fig.9.9. It is compared with experimental values of argon and neon; for which the intermolecular pair potential is a function of the interparticle separation. The agreement is good. At high temperature ($T^* \gg 1$), where the repulsive part of the interaction dominates, the virial coefficient B_2^* is positive. However, at low temperature ($T^* \ll 1$), where the attractive part of interaction dominates, the virial coefficient is negative. The temperature at which $B_2^* = 0$ is called the Boyle's temperature T_B, which is found to be $T_B^* = kT_B/\epsilon = 3.42$ for the Lennard-Jones (12-6) potential.

Determination of higher virial coefficients for the lennard-Jones (12-6) model is much more complicated and is not attempted here.

(iii) Dipolar hard sphere model

For calculating the second virial coefficient of dipolar hard sphere molecules we write (9.4.14) in the form

$$u(r\omega_1\omega_2) = u_{HS}(r) + u_l(r\omega_1\omega_2) \quad (9.5.17)$$

where $u_{HS}(r)$ is the hard sphere potential, defined by (9.4.9) and $u_l(r\omega_1\omega_2)$ is

$$u_l(r\omega_1\omega_2) = -(\mu^2/r^3)\, g(\theta_1,\theta_2,\phi) \quad (9.5.18)$$

where $\phi = \phi_2 - \phi_1$.

Substituting (9.5.17) in (9.3.16) and expanding $\exp(-u_l/kT)$ in power series in (1/kT), we get

$$B_2 = -2\pi \int_0^{\sigma} \exp[-\beta u_{HS}(r)] - 1) r^2 dr - (1/4) \int_{\sigma}^{\infty} \int \exp[-\beta u_{HS}(r)] \left(-\sum_{i=1}^{\infty} (1/n!)(-u_l/kT)^n\right)$$

$$r^2 dr \sin\theta_1 d\theta_1 \sin\theta_2 d\theta_2 d\phi$$

when the integration over the angles is performed, the odd power of (1/kT) terms are zero. Then the final result is

$$B_2 = (2\pi\sigma^3/3)\left[1 - \sum_{n=1}^{\infty} (a_{2n}/(2n)!(2n-1))(\mu^{*2})^{2n}\right] \quad (9.5.19)$$

where $\mu^{*2} = \mu^2/\sigma^3 kT$ and a_{2n} is defined as

$$a_{2n} = (1/8\pi) \int_0^{2\pi} \int_0^{\pi} \int_0^{\pi} [g(\theta_1\, \theta_2\, \phi)]^{2n} \sin\theta_1 d\theta_1 \sin\theta_2 d\theta_2 d\phi \quad (9.5.20)$$

The values of a_{2n} for the first few values of n are given as $a_2=2/3$, $a_4=24/25$ and $a_6=464/245$. Thus, B_2 for the dipolar hard sphere gas is expressed as

$$B_2 = (2\pi\sigma^3/3)[1 - (1/3)(\mu^{*2})^2 - (1/75)(\mu^{*2})^4 - (29/55125)(\mu^{*2})^6 - \ldots] \quad (9.5.21)$$

This is monatomically decreasing function of μ^{*2}. In (9.5.21), the first term is the second virial coefficient of the hard sphere gas and other terms are corrections due to the dipole moment.

(iv) Stockmayer potential model

In this case Eq.(9.4.14) can be written as

$$u(r\omega_1\omega_2) = u_{LJ}(r) + u_l(r\omega_1\omega_2) \quad (9.5.22)$$

where $u_{LJ}(r)$ is the Lennard-Jones (12-6) potential given by (9.4.11) and $u_l(r\omega_1\omega_2)$ is given by (9.5.18).

Substituting (9.5.22) in (9.3.16) and expanding $\exp(-u_l/kT)$ in power series in (1/kT) we get

$$B_2 = B_2(LJ) - (1/4) \int_0^{\infty} \exp[-\beta u_{LJ}(r)] \left(-\sum_{n=1}^{\infty} (1/n!)(-u_l/kT)^n\right) r^2 dr \sin\theta_1 d\theta_1 \sin\theta_2 d\theta_2 d\phi \quad (9.5.23)$$

Here the odd power of (1/kT) terms are zero on integrating over the angles. In order to solve (9.5.23), we use the following reduced quantities

$$B_2^* = B_2/(2\pi\sigma^3/3)\ ;\ T^* = kT/\epsilon\ ;\ \mu^{*2} = \mu^2/\epsilon\sigma^3\ ;\ t^* = \mu^{*2}/(8)^{1/2}\ ;\ r^* = r/\sigma \quad (9.5.24)$$

Then (9.5.23) can be written as

$$B_2^* = B_2^*(LJ) - 3\sum_{n=1}^{\infty} (a_{2n}/(2n)!)\,(\mu^{*2}/T^*)^{2n} I_{2n}$$

$$= B_2^*(LJ) - (\mu^{*2}/T^*)^2 B_2^{2*} - (\mu^{*2}/T^*)^4 B_2^{4*} - (\mu^{*2}/T^*)^6 B_2^{6*} + \ldots \quad (9.5.26)$$

where $B_2^*(LJ)$ is the reduced second virial coefficient of the Lennard-Jones fluid and B_2^{2*}, B_2^{4*}, B_2^{6*} - ... are the second, fourth and sixth order correction terms due to the dipole dipole interaction. They are given by

$$B_2^{2*} = I_2 \quad (9.5.27a)$$

$$B_2^{4*} = (3/25)\, I_4 \quad (9.5.27b)$$

$$B_2^{6*} = (29/3675)\, I_6 \quad (9.5.27c)$$

where

$$I_{2n} = \int_0^{\infty} \exp\left[-(4/T^*)\,(r^{*-12} - r^{*-6})\right] (r^*)^{-6n+2}\, dr^* \quad (9.5.28)$$

Equation (9.5.28) can be evaluated numerically. It can also be solved analytically when $\exp(4r^{*6}/T^*)$ expanded in an infinite series. Following the method of solving (9.5.12), (9.5.28) can be solved as

$$I_{2n} = \Sigma(1/12i!)\,(4/T^*)^{(2i-2n+1)/4}\,\Gamma((2i+2n-1)/4) \quad (9.5.29)$$

where $\Gamma(l)$ is the gamma function.

The reduced second virial coefficient B_2^* depends on the reduced temperature T^* as well as reduced dipole moment μ^*. B_2^* is plotted as a function of T^* in Fig.9.10 for many values of t*. We find that the B_2^* curve of polar molecules lies beneath that of non-polar gases.

9.6. Equation of State for Hard Sphere Fluid

The equation of state for a dense hard-sphere fluid can be calculated using the known virial coefficients. If N be the number of hard spheres of diameter d in a volume V, then the packing fraction η is defined by

$$\eta = Nv/V$$

where $v = (\pi/6)d^3$ is the volume of a hard sphere. Hence η can be expressed as

$$\eta = (\pi/6)\rho d^3$$

where $\rho = N/V$ is the number density, then the equation of state for a hard sphere fluid can be expressed as

$$\beta P/\rho = 1 + \sum_{l=1}^{\infty} {}_l\eta^l \quad (9.6.1)$$

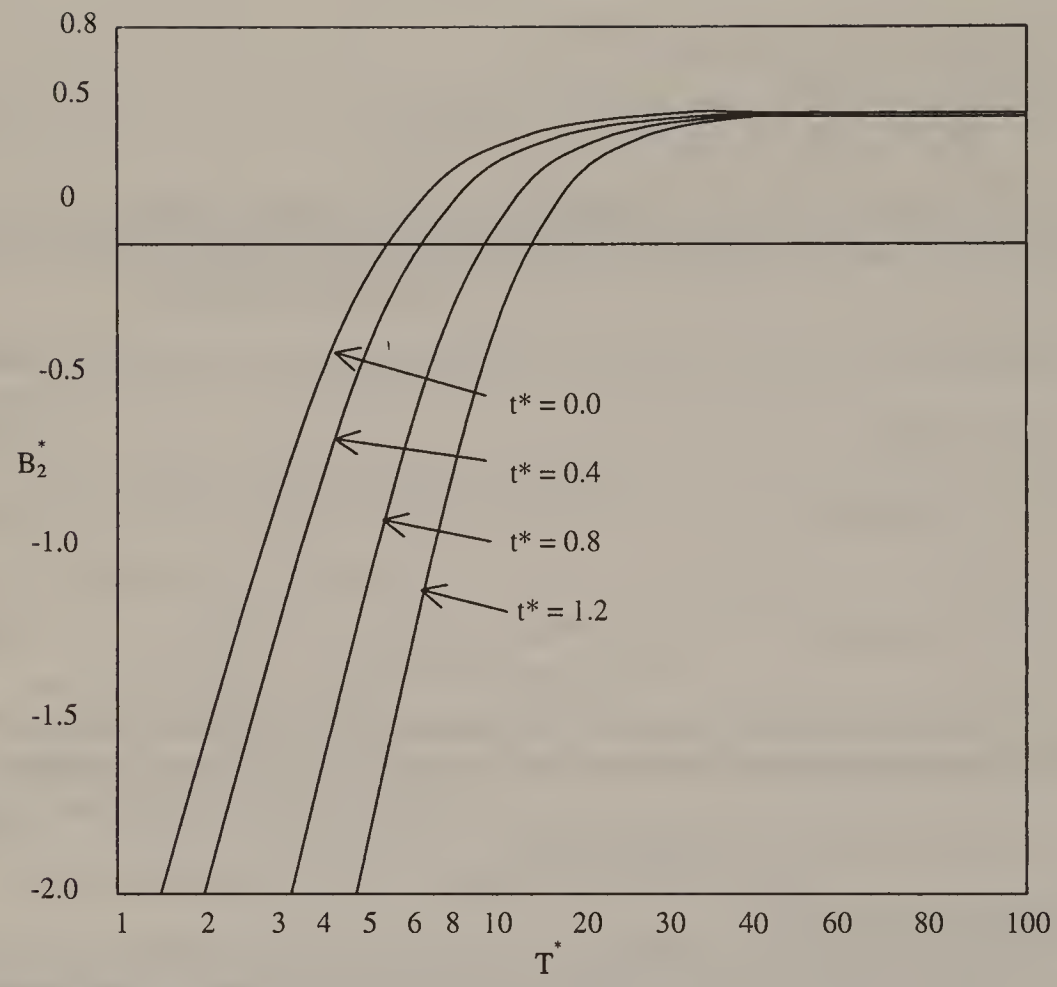


Fig.9.10. The reduced second virial coefficient B_2^* as a function of T^* for different t^* for the Stockmayer potential model

where

$$_l = (6/\pi d^3)^l B_{l+1} = (4/b_0)^l B_{l+1} \qquad (9.6.2)$$

Substituting the numerical values of B_{l+1}, Eq.(9.6.1) can be written as

$$\beta P/\rho = 1 + 4\eta + 10\eta^2 + 18.36\eta^3 + \ldots \qquad (9.6.3)$$

Carnahan and Starling (1969), being guided by (9.6.3), have derived an equation of state for hard spheres which agrees with exact results very accurately. To derive the theory, they replace $_4$ by the closest integral 18 and write $_l$ in the form

$$_l = \alpha_0 + \alpha_1 l + \alpha_2 l^2 \qquad (9.6.4)$$

where α_0, α_1 and α_2 are constants and can be evaluated using the first three values of $_l$, i.e.

$$_1 = 4 ; \qquad _2 = 10 ; \qquad _3 = 18$$

Thus, we get

$$\alpha_0 + \alpha_1 + \alpha_2 = 4 \tag{9.6.5a}$$

$$\alpha_0 + 2\alpha_1 + 4\alpha_2 = 10 \tag{9.6.5b}$$

$$\alpha_0 + 3\alpha_1 + 9\alpha_2 = 18 \tag{9.6.5c}$$

These equations can be solved to give

$$\alpha_0 = 0 \; ; \qquad \alpha_1 = 3 \; ; \qquad \alpha_2 = 1 \tag{9.6.6}$$

Thus, we get

$$_l = 3l + l^2 \tag{9.6.7}$$

and

$$\beta P/\rho = 1 + \sum_{l=1}^{\infty} (3l + l^2)\eta^l \tag{9.6.8}$$

which can be expressed explicitly in a simple form as

$$\beta P/\rho = (1 + \eta + \eta^2 - \eta^3)/(1-\eta)^3 \tag{9.6.9}$$

The Carnahan-Starling (CS) equation of state for the hard sphere fluid agrees remarkably well with the exact results over a wide density range. The result for the equation of state for the hard sphere fluid is reported in Table 9.2.

Table 9.2. The Equation of state, $\beta P/\rho$ and Excess Free Energy per Particle, βf of the Hard Sphere Fluid.

η	$\beta P/\rho$	βf
0.05	1.227	0.213
0.10	1.521	0.457
0.15	1.904	0.737
0.20	2.406	1.063
0.25	3.074	1.444
0.30	3.974	1.898
0.35	5.206	2.444
0.40	6.926	3.111
0.45	9.385	3.942
0.50	13.000	5.000

It can be conveniently used to calculate the other thermodynamic properties of the system. For example, the excess free energy with respect to the ideal gas, $A^{Ex} = A - A^{id}$, for the hard sphere fluid can be derived using (9.6.9) in the relation

$$\beta f = (\beta A^{Ex}/N) = \int_0^{\eta} [(\beta P/\rho) - 1]\,(d\eta'/\eta') = \eta(4 - 3\eta)/(1 - \eta)^2 \tag{9.6.10}$$

The results for the excess free energy per particle, βf, is also listed in Table 9.2.

9.7. Radial Distribution Function

We consider a classical monatomic fluid of N identical molecules in a volume V and temperature T. Assuming the total interaction potential to be pairwise additive, the l-particle density distribution function is given by [see Eq.(4.8.13)]

$$n_N(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_l) = (N!/(N-l)!\,Z_N) \int \ldots \int \exp\Big[-\sum_{i<j} u(\mathbf{r}_i,\mathbf{r}_j)/kT\Big] \prod_{i=l+1}^{N} d\mathbf{r}_i \tag{9.7.1}$$

The most important distribution function is $n_N(\mathbf{r}_1, \mathbf{r}_2)$. The quantity $n_N(\mathbf{r}_1, \mathbf{r}_2)d\mathbf{r}_1\, d\mathbf{r}_2$ is the probability that one particle of the system is in $d\mathbf{r}_1$ at $\mathbf{r}_1$ and another in $d\mathbf{r}_2$ at $\mathbf{r}_2$. A fluid exhibits short range order, i.e. there is no correlation between particles when they are far apart. Thus, for a system of non-interacting particle, (9.7.1) becomes

$$n_N(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_l) \approx n_N(\mathbf{r}_1)\, n_N(\mathbf{r}_2)\, n_N(\mathbf{r}_l) = \rho^l \tag{9.7.2}$$

The effect of the interaction potential is to cause deviations of the distribution function about the mean value. Thus one can define a function $g(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_l)$ by

$$n_N(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_l) = \Big(\prod_{i=1}^{l} n_N(\mathbf{r}_i)\Big)\, g(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_l) \qquad \text{for} \geq 2 \tag{9.7.3}$$

For a homogeneous fluid, where $n_N(\mathbf{r}_1) = n_N(\mathbf{r}_2) = \ldots \equiv \rho$, (9.7.3) takes the form

$$n_N(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_l) = \rho^l g(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_l) \qquad \text{for} \geq 2 \tag{9.7.4}$$

The function $g(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_l)$ is known as the l-particle correlation function. $g(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_l)$ is dimensionless and represents the relative probability of finding the subset of l-particles in the configuration $\{\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_l\}$. The most important correlation function is the pair correlation function $g(\mathbf{r}_1,\mathbf{r}_2)$.

From (9.7.1), we obtain the following recurrence relation between two and three-particle correlation functions

$$g(\mathbf{r}_1,\mathbf{r}_2) = (\rho/(N-2)) \int g(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)\, d\mathbf{r}_3 \tag{9.7.5}$$

For a homogeneous fluid of spherical particles $g(\mathbf{r}_1, \mathbf{r}_2)$ depends only on the interparticle separation $r \equiv |\mathbf{r}_1 - \mathbf{r}_2|$, i.e.

$$g(\mathbf{r}_1, \mathbf{r}_2) = g(r)$$

g(r) is called the radial distribution function (RDF), which satisfies the normalization condition

$$g(r) \to 1 \qquad \text{as } r \to \infty \tag{9.7.6}$$

A typical RDF g(r) shown in Fig.9.11

The physical interpretation of g(r) for a simple fluid can be given in the following way. We consider one particle to be fixed at $\mathbf{r}_1$, then the probability of observing a second particle in $d\mathbf{r} \equiv d\mathbf{r}_{12}$ at $\mathbf{r}_2$ is the number of particles dN in the spherical shell of radius r and thickness dr, about the fixed particles at $\mathbf{r}_1$. Thus,

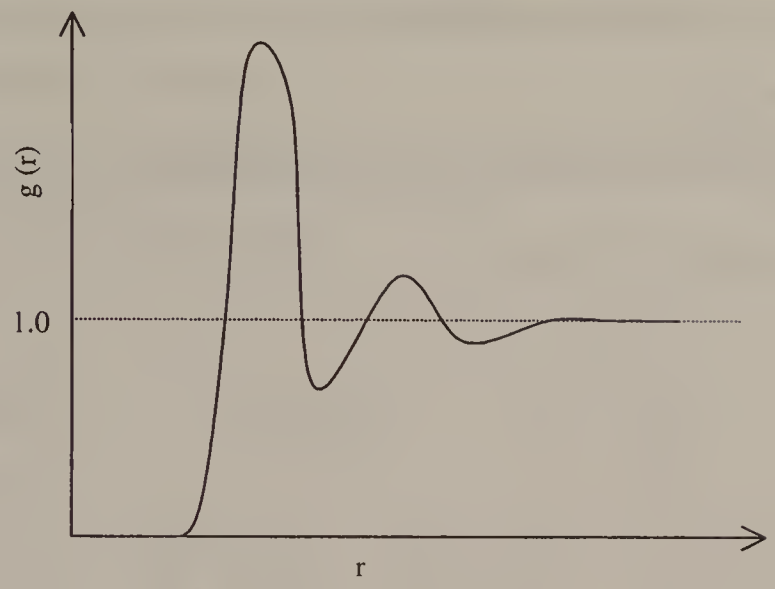


Fig.9.11. A typical radial distribution function g(r) as a function of r.

$$dN = \rho g(r) 4\pi r^2 \, dr \tag{9.7.7}$$

and integrating over the volume V, we have

$$4\pi\rho \int g(r) r^2 \, dr = N - 1 \tag{9.7.8}$$

We use another correlation function $h(\mathbf{r}_1, \mathbf{r}_2)$ defined by the relation

$$h(\mathbf{r}_1, \mathbf{r}_2) = g(\mathbf{r}_1, \mathbf{r}_2) - 1 \tag{9.7.9}$$

which is known as total pair correlation function. This function is a measure of the total influence of the molecule '1' on another molecule '2' at a distance r_{12}. Ornstein and Zernike (1914) proposed the division of $h(\mathbf{r}_1, \mathbf{r}_2)$ into two parts: a direct correlation function $c(\mathbf{r}_1, \mathbf{r}_2)$ and an indirect part. The indirect part is an influence of particle '1' on a third particle '3' with the consequent influence of '3' on '2'. This effect is weighted with the density and average over all positions of molecule '3'. That is,

$$h(\mathbf{r}_1, \mathbf{r}_2) = c(\mathbf{r}_1, \mathbf{r}_2) + \rho \int c(\mathbf{r}_1, \mathbf{r}_3) \, h(\mathbf{r}_3, \mathbf{r}_2) \, d\mathbf{r}_3 \tag{9.7.10}$$

This equation is usually known as Ornstein-Zernike (OZ) equation. The Eq.(9.7.10) can be iterated in such a way so as to replace the right hand side by an infinite series of c, i.e

$$h(\mathbf{r}_1, \mathbf{r}_2) = c(\mathbf{r}_1, \mathbf{r}_2) + \rho \int c(\mathbf{r}_1, \mathbf{r}_3) \, c(\mathbf{r}_3, \mathbf{r}_2) \, d\mathbf{r}_3 + \rho^2 \int c(\mathbf{r}_1, \mathbf{r}_3) \, c(\mathbf{r}_3, \mathbf{r}_4) \, c(\mathbf{r}_4, \mathbf{r}_2) \, d\mathbf{r}_3 \, d\mathbf{r}_4 + \ldots \tag{9.7.11}$$

We can, of course, obtain a similar expansion for the direct correlation function $c(\mathbf{r}_1, \mathbf{r}_2)$ in terms of h-bonds.

$$c(\mathbf{r}_1, \mathbf{r}_2) = h(\mathbf{r}_1, \mathbf{r}_2) - \rho \int h(\mathbf{r}_1, \mathbf{r}_3) \, h(\mathbf{r}_3, \mathbf{r}_2) \, d\mathbf{r}_3 + \rho \int h(\mathbf{r}_1, \mathbf{r}_3) \, h(\mathbf{r}_3, \mathbf{r}_4) \, h(\mathbf{r}_4, \mathbf{r}_2) \, d\mathbf{r}_3 \, d\mathbf{r}_4 + \ldots \tag{9.7.12}$$

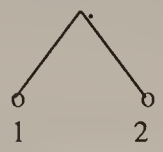
In the low density limit $\rho \to 0$, the RDF $g(\mathbf{r}_1, \mathbf{r}_2)$ reduces to

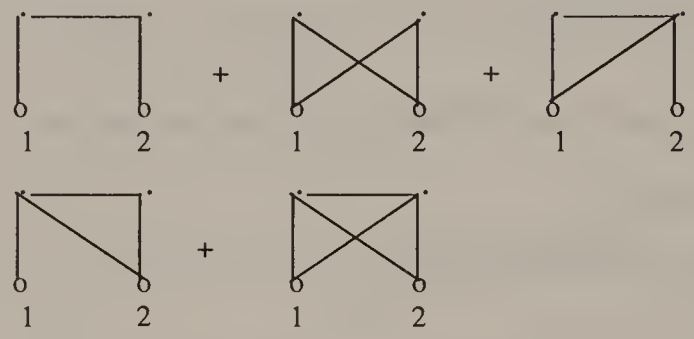
$$g(\mathbf{r}_1, \mathbf{r}_2) \underset{\rho \to 0}{=} \exp\,[-\beta u(\mathbf{r}_1, \mathbf{r}_2)/kT\,] \tag{9.7.13}$$

It is, therefore, convenient to express the density expansion of $g(\mathbf{r}_1, \mathbf{r}_2)$ in the form

$$g(\mathbf{r}_1, \mathbf{r}_2) = \exp\,[-u(\mathbf{r}_1, \mathbf{r}_2)/kT\,]\,[1 + \sum_{n=1}^{\infty} \rho^n g_n(\mathbf{r}_1, \mathbf{r}_2)] \tag{9.7.14}$$

where

$\rho g_1(\mathbf{r}_1, \mathbf{r}_2)$ =  $= \rho \int f_{13}\, f_{23}\, d\mathbf{r}_3$ (9.7.15)

$\rho^2 g_2(\mathbf{r}_1, \mathbf{r}_2)$ = 

(9.7.16)

and so on. These are the general expressions for $g_1(\mathbf{r}_1, \mathbf{r}_2)$ and $g_2(\mathbf{r}_1, \mathbf{r}_2)$ in terms of f-bonds and black ρ-circles, which have integration over $d\mathbf{r}$. Thus

$$\bullet \equiv \int [\bigcirc_1]\, d\mathbf{r}_i = \rho \int d\mathbf{r}_i$$

where the white circle has a vertex function ρ.

For a hard sphere fluid, $g_1(r)$ can be evaluated in the form (9.5.7) as

$$g_1^{HS}(r) = (4\pi d^3/3)\,[1 - (3/4)\,(r/d) + (1/16)(r/d)^3], \qquad d \le r \le 2d$$

$$= 0, \qquad r \ge 2d \tag{9.7.17}$$

and in the low density limit,

$$g^{HS}(r) = 0, \qquad r < d$$

$$= 1 + (4\pi/3)(\rho d^3)\,[1 - (3/4)\,(r/d) + (1/16)(r/d)^3], \qquad d < r < 2d$$

$$= 1, \qquad r > 2d \tag{9.7.18}$$

The RDF $g^{HS}(r)$ for the hard sphere gas is shown in Fig.9.12 at $\rho d^3 = 0$ and 0.5. In the range $d < r < 2d$, $g^{HS}(r)$ is greater than unity. This is attributed to an effective mean attractive force between molecules 1 and 2 arising from the remaining $N - 2$ molecules.

It is useful to relate g(r) to the potential of mean force $\psi(r)$ by

$$\psi(r) = -kT \ln g(r) \tag{9.7.19}$$

In the limit $\rho \to 0$, $\psi(r)$ becomes equal to the pair interaction potential u(r). The difference between u(r) and $\psi(r)$ can be written as

$$W(r) = \beta[u(r) - \psi(r)] \tag{9.7.20}$$

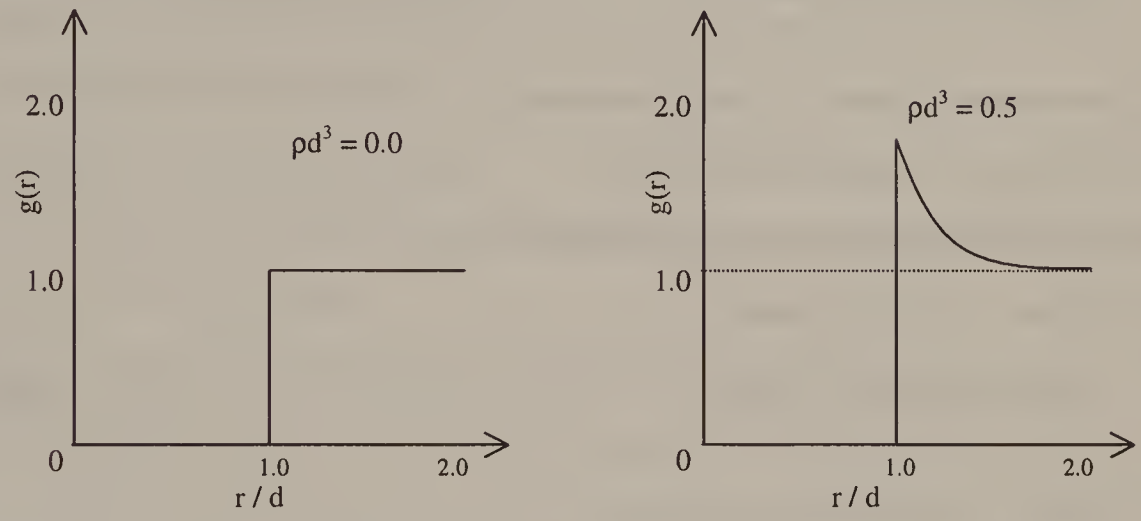


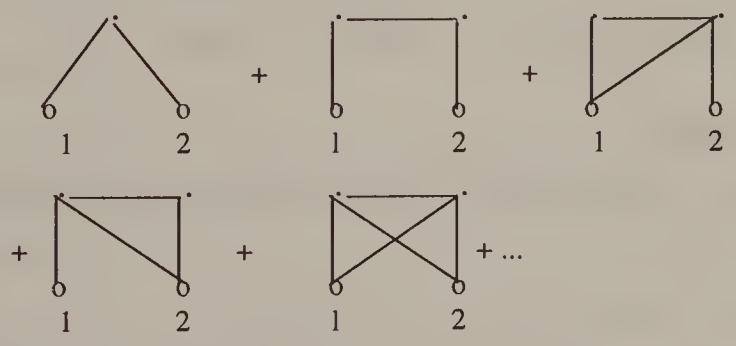
Fig.9.12. The radial distribution function g(r) for a hard sphere fluid according to Eq.(9.7.18) at $\rho d^3 = 0$ and 0.5.

so that

$$e^{W(r)} = g(r)\, e^{\beta u(r)} = y(r) \tag{9.7.21}$$

where $W(\mathbf{r}_1,\mathbf{r}_2)$ is the logarithm of expression in brackets on the right hand side of Eq.(9.7.19). Thus

$W(\mathbf{r}_1,\mathbf{r}_2) =$



(9.7.22)

9.8. Application to One-Component Plasma

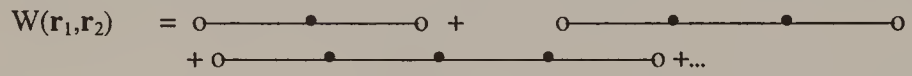
As an illustration, we now apply the cluster expansion technique to calculate the RDF of a uniform one-component plasma of point charge q. The pair potential in this case is given by

$$u(r) = q^2/r \tag{9.8.1}$$

and the Mayer function f is

$$f(r) = \exp(-\beta q^2/r) - 1 \tag{9.8.2}$$

In order to calculate g(r), one should sum all diagram appearing in the expansion of W(r). However, the series may diverse. So, we sum only the chain diagrams to all orders in ρ and neglect all other diagrams. Thus the function $W(\mathbf{r}_1,\mathbf{r}_2)$ is expressed in the approximate form as



(9.8.3)

which can be expressed in terms of a convolution integral as

$$W(\mathbf{r}_1, \mathbf{r}_2) = \rho \int f_{13} [f_{32} + W(\mathbf{r}_3, \mathbf{r}_2)] \, d\mathbf{r}_3 \tag{9.8.4}$$

Taking the Fourier transform, it can be written in the form

$$\hat{W}(\mathbf{k}) = \rho [\hat{f}(\mathbf{k})]^2 + \rho \hat{f}(\mathbf{k})\hat{W}(\mathbf{k}) \tag{9.8.5}$$

or

$$\hat{W}(\mathbf{k}) = \rho [\hat{f}(\mathbf{k})]^2 / (1 - \rho \hat{f}(\mathbf{k})) \tag{9.8.6}$$

where

$$\hat{f}(\mathbf{k}) = \int \exp[-i\mathbf{k}.\mathbf{r}] [\exp(-\beta q^2/r) - 1] d\mathbf{r}$$

$$-\beta q^2 \int (\exp[-i\mathbf{k}.\mathbf{r}]/r) \, d\mathbf{r} \tag{9.8.7}$$

Using the spherical polar coordinates (r, θ, φ), Eq.(9.8.7) can be integrated to give

$$\hat{f}(\mathbf{k}) = -2\pi\beta q^2 \int_0^\infty dr\, r \int_0^\pi e^{-ikr\cos\theta} \sin\theta \, d\theta$$

$$= -(4\pi\beta q^2/k) \int_0^\infty dr \sin kr = -4\pi\beta q^2/k^2 = -k_D^2/\rho k^2 \tag{9.8.8}$$

where

$$k_D = (4\pi\beta\rho q^2)^{1/2} \tag{9.8.9}$$

is called the Debye wave number and $\Lambda_D = 1/k_D$ is the Debye screening length. Then from (9.8.6) and (9.8.9), we find

$$\beta\rho \hat{\Psi}(\mathbf{k}) = \rho [\beta \hat{u}(\mathbf{k}) - \hat{w}(\mathbf{k})] \quad -\rho [\hat{w}(\mathbf{k}) + \hat{f}(\mathbf{k})]$$

$$= \rho \hat{f}(\mathbf{k}) / (1 - \rho \hat{f}(\mathbf{k})) = k_D^2/(k_D^2 + k^2) \tag{9.8.10}$$

Taking the inverse Fourier transform we get

$$\beta\rho\Psi(r) = (1/(2\pi)^3) \int \exp[-i\mathbf{k}.\mathbf{r}] [k_D^2/(k_D^2 + k^2)] dk$$

$$= (k_D^2/(2\pi)^3) \int_0^{\infty} (k^2/(k_D^2 + k^2))\, dk \int_0^{\pi} \exp[ikr\cos\theta] \sin\theta\, d\theta$$

$$= (k_D^2/2\pi^2 r) \int_0^{\infty} (k \sin kr/(k_D^2 + k^2))\, dk$$

$$= (k_D^2/4\pi r) \exp[-k_D r]$$

or

$$\beta\rho\Psi(r) = -(\beta q^2/r) \exp[-k_D r] \qquad (9.8.11)$$

From (9.7.19) the RDF g(r) is given by

$$g(r) = \exp[-(\beta q^2/r) \exp(-k_D r)] \qquad (9.8.12)$$

Thus we find that the summation of the chain diagrams gives a renormalised pair potential

$$C(r) = (q^2/r) \exp(-k_D r) \qquad (9.8.13)$$

where the Coulomb potential is damped by the factor $\exp(-k_D r)$, which corresponds to the screening effect.

Retaining only the first term of (9.8.12) gives the linearised Debye-Huckel form for g(r).

$$g(r) \quad 1 - (\beta q^2/r) \exp(-k_D r) \qquad (9.8.14)$$

which is valid $r \ll \Lambda_D$, and was given by Debye and Huckel (1923). Except for very small k_D, the Debye-Huckel theory gives poor results.

Problems

9.1 Calculate the deviation due to the interaction between molecules to the equation of state of a rarefied gas whose molecules interact via the pair potential

$u(r) = \infty \qquad r < d$

$= \alpha/r^n \qquad r > d$

where α is a constant quantity.

9.2 Explain, with special reference to the van der Waals equation of state, what is meant by the principle of corresponding state, and obtain the reduced equation of state.

9.3 Show that the specific heat at constant volume C_v of a van der Waals gas is a function of temperature only.

9.4 Derive the Maxwell construction by minimizing the Helmholtz free energy.

9.5 Show that, for a gas obeying van der Waals equation of state

$C_P - C_V = Nk[1 - (2a/NkTV^3)(V-b)^2]^{-1}$

9.6 Calculate b_2 and b_3 for a hard sphere gas with hard sphere diameter d.

9.7 Express the equation of state of a hard sphere gas in the virial form, including terms up to the third virial coefficient.

9.8 Show that the second virial coefficient of a binary mixture with concentration x_1 and x_2 can be written as

$B_2 = [x_1^2 B_{11} + 2x_1x_2B_{12} + x_2^2 B_{22}]$

where

$B_{\alpha\gamma} = -(1/2) \int [\exp(-\mu_{\alpha\gamma}(r)/kT) - 1]\, d\mathbf{r}$

Using this expression, calculate the virial coefficient for the binary mixture of hard spheres of diameter d_{11} and d_{22}. [Use combination rule $d_{12} = (d_{11}+d_{22})/2$].

9.9 Calculate the second virial coefficient of a gas, obeying Sutherland potential defined by

$u(r) = \infty \qquad r < d$

$= -\epsilon (d/r)^6 \qquad r > d$

9.10 Molecules of a gas are interacting via the square-well potential

$u(r) = \infty \qquad r < d$

$= -\epsilon \qquad d < r < \lambda d$

$= 0 \qquad r < \lambda d$

Use this potential model to calculate the second and third virial coefficients of the gas.

9.11 Find the second virial coefficient of an anharmonic oscillator with potential energy

$U(x) = (1/2)(\alpha x^2 + \gamma x^4)$

9.12 Calculate the lowest order corrections to the ideal-gas values of the thermodynamic properties of a real gas with the square-well potential.

CHAPTER 10

QUANTUM STATISTICAL MECHANICS OF INTERACTING SYSTEMS

Most of the fluids on the surface of the earth can be treated classically because the thermal de Broglie wavelength

$$\lambda = (2\pi\beta\hbar^2/m)^{1/2}$$

associated with a particle is considerably smaller than the mean particle spacing

$$l = (6/\pi\rho)^{1/3}$$

where $\rho = N/V$ is the number density. There are some fluids for which deviations from classical behaviour are observed at low temperatures. Notable among them are liquid He^4 and He^3, hydrogen and neon.

The importance of this deviation increases with decreasing molecular weight. The deviations arise due to two quantum effects.

(i) Diffraction effects, which are linked with the wave nature of the particles.

(ii) Exchange effects, which are due to statistics (Bose-Einstein and Fermi-Dirac) obeyed by the particles.

The exchange (or symmetry) effects are very small for all fluids except liquid helium below 5 K (Boyd et al., 1969). On the other hand, the diffraction effects are appreciable even at high temperatures.

The deviations from the classical behaviour depend on the magnitude of a dimensionless parameter Λ^* defined as

$$\Lambda^* = (h/\sigma)\sqrt{(m\epsilon)}$$

where ϵ and σ are, respectively, measures of the strength and range of interaction potential. Essentially, Λ^* is measure of the ratio of the de Broglie wavelength of the relative motion of two molecules with relative kinetic energy ϵ, to the diameter σ of the molecule. Some typical results are listed in Table 10.1 for ϵ, σ and Λ^*.

This chapter deals with the calculation of these quantum effects on the thermodynamic properties of systems.

10.1. Cluster Expansion for Quantum Systems

The cluster expansion of Kahn and Uhlenbeck (1938) and its elaboration by Lee and Young (1959, 1960) is perhaps the most natural method for the treatment of a quantum system. The basic approach in

this theory is to evolve a scheme to expand the Slater sum of the system in essentially the same way as one obtains the cluster expansion of the Boltzmann factor of a classical fluid. However, because of the interplay of two effects of quantum statistics and particle dynamics arising from the interparticle interactions, the mathematical structure of this theory is considerably involved. In this section, we discuss the method of separating these effects.

Table 10.1. Values of the Lennard-Jones (12-6) Force Parameters and Quantum Parameter.

Systems	ϵ/k(K)	σ(A)	Λ^*
He	10.22	2.556	2.67(^{4}He)
			3.08(^{3}He)
Ne	35.60	2.749	0.593
Ar	119.80	3.405	0.186
H_2	37.00	2.928	1.729
D_2	37.00	2.928	1.223
N_2	95.05	3.698	0.226
O_2	117.50	3.580	2.201

We consider a quantum mechanical system of N identical particles, each of mass m, enclosed in a container of volume V in equilibrium at temperature T. The Hamiltonian operator $\hat{H}_N$ of the system is

$$\hat{H}_N = -(\hbar^2/2m) \sum_{i=1}^{N} \nabla_i^2 + \sum_{i<j} u(\mathbf{r}_i, \mathbf{r}_j) \tag{10.1.1}$$

where $u(\mathbf{r}_i, \mathbf{r}_j)$ is the pair interaction potential between molecules i and j. Then, the partition function for the quantum system is given by [see Eq.(4.9.2)].

$$Q_N = \text{tr} \exp(-\beta \hat{H}_N) = \int \cdots \int \sum_x \psi_x^*(1, \ldots, N) \exp(-\beta \hat{H}_N) \psi_x(1, \ldots, N) \prod_{i=1}^{N} d\mathbf{r}_i \tag{10.1.2}$$

where ψ_x is a complete set of (properly symmetrized, or antisymmetrized according to statistics) orthonormal wave functions for the system under consideration, and the number 1, 2, ..., N denote the position coordinates $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N$, respectively.

We now introduce a quantity, known as the probability density matrix defined as

$$W_N^{S/A}(1', \ldots, N'; 1, \ldots, N) = N! \lambda^{3N} \sum_x \psi_x^*(1', \ldots, N') \exp(-\beta \hat{H}_N) \psi_x(1, \ldots, N) \tag{10.1.3}$$

where the superscripts S or A denote the fact that the function ψ_x is properly symmetrized or antisymmetrized, respectively, according to statistics (Bose-Einstein or Fermi-Dirac). Its diagonal element is known as the Slater sum $W_N^{S/A}(1, 2, \ldots, N)$. Thus

$$W_N^{S/A}(1, 2, \ldots, N) = W^{S/A}(1, \ldots, N; 1, \ldots, N)$$

$$= N! \lambda^{3N} \sum_x \psi_x^*(1, \ldots, N) \exp(-\beta \hat{H}_N) \psi_x(1, \ldots, N) \tag{10.1.4}$$

Then Eq.(10.1.2) takes the form

$$Q_N = (1/N!\lambda^{3N}) \int \ldots \int W_N^{S/A}(1, 2, \ldots, N) \prod_{i=1}^{N} dr_i = (1/N!\lambda^{3N})\, tr\,(\exp(-\beta \hat{H}_N) \quad (10.1.5)$$

The thermodynamic properties of the system can be obtained from Q_N. Thus, the Helmholtz free energy is

$$\beta A = -\ln Q_N \quad (10.1.6)$$

and the pressure is

$$\beta P = -\partial \ln Q_N / \partial V \quad (10.1.7)$$

One can also use the grand partition function Ξ of the system defined as

$$\Xi = \sum_{N=1}^{\infty} (z^N/N!) \int \ldots \int W^{S/A}(1, 2, \ldots, N) \prod_{i=1}^{N} dr_i \quad (10.1.8)$$

where z is a complex number, known as quantum fugacity. The pressure P and the number density ρ of the system are given by the relations

$$\beta P = \lim_{V \to \infty} V^{-1} \ln \Xi \quad (10.1.9)$$

$$\rho = V^{-1} z\, (\partial \ln \Xi / \partial z) \quad (10.1.10)$$

The cluster expansion of the probability density matrix

We express the function $W_N^{S/A}$ in terms of the cluster function $U_l^{S/A}$, which is the quantum mechanical analogue of the classical Ursell function U_l. Thus

$$W_1^{S/A}(1',1) = U_1^{S/A}(1',1) \quad (10.1.11a)$$

$$W_2^{S/A}(1',2';1,2) = U_1^{S/A}(1';1)\, U_1^{S/A}(2';2) + U_2^{S/A}(1',2';1,2) \quad (10.1.11b)$$

$$W_3^{S/A}(1',2',3';1,2,3) = U_1^{S/A}(1';1)\, U_1^{S/A}(2';2)\, U_1^{S/A}(3',3) + U_1^{S/A}(1';1)\, U_2^{S/A}(2',3';2,3) + U_1^{S/A}(2';2)\, U_2^{S/A}(1';3';1,3) + U_1^{S/A}(3';3)\, U_2^{S/A}(1';2';1,2) + U_3^{S/A}(1',2',3';1,2,3) \quad (10.1.11c)$$

$$W_N^{S/A}(1', \ldots, N'; 1, \ldots, N) = U_1^{S/A}(1,1) \ldots U_1^{S/A}(N';N) + \ldots + U_N^{S/A}(1',\ldots,N';1,\ldots,N) \quad (10.1.11d)$$

The function $U_l^{S/A}$ is the contribution due to all l-particles close to one another; $U_l^{S/A} = 0$ unless the

particles are clustered. The general expression for $W_N^{S/A}$ in terms of the cluster function $U_l^{S/A}$ is given by

$$W_N^{S/A} = \sum_{\{m_l\}} \sum_{P} [[\, U_1^{S/A} \ldots U_1^{S/A}] \; [U_2^{S/A} \ldots U_2^{S/A}] \ldots U_N^{S/A}] \tag{10.1.12}$$

(m_1 m_2 m_N)

where the first summation goes over all the sets $\{m_l\}$ which satisfies the condition

$$\sum_{i=1}^{N} l m_i = N \tag{10.1.13}$$

The second sum $\sum_P$ denotes a summation over all distinct ways of selecting the arguments under the sets $\{m_l\}$.

The $U_l^{S/A}$ can be also be expressed in terms of the $W^{S/A'}$s. From (10.1.11) we get

$$U_1^{S/A}(1';1) = W_1^{S/A}(1';1) \tag{10.1.14a}$$

$$U_2^{S/A}(1',2';1,2) = W_2^{S/A}(1',2';1,2) - W_1^{S/A}(1';1)\, W_1^{S/A}(2';2) \tag{10.1.14b}$$

$$\begin{aligned} U_3^{S/A}(1',2',3';1,2,3) = {} & W_3^{S/A}(1',2',3';1,2,3) - W_1^{S/A}(1';1)\, W_2^{S/A}(2',3';2,3) \\ & - W_1^{S/A}(2';2)\, W_2^{S/A}(1',3';1,3) - W_1^{S/A}(3';3)\, W_2^{S/A}(1',2';1,2) \\ & + 2W_1^{S/A}(1';1)\, W_1^{S/A}(2',2)\, W_1^{S/A}(3';3) \end{aligned} \tag{10.1.14c}$$

and so on. Since $W_l^{S/A}$ possesses the product property, it follows from the above equations that $U_l^{S/A}$ will have the cluster property.

The effects of interaction and statistics are both entangled in $U_l^{S/A}$. The function $U_l^{S/A}$ can, in principle, be found from the solution of the quantum mechanical l-body problem. However, there is no general method for calculation of $U_l^{S/A}$ except for l = 1, 2. In case of l = 1, one can easily show that

$$\begin{aligned} W_1^{S/A}(1',1) &= \lambda^3 \langle 1' | \exp(-\beta \hat{H}_1) | 1 \rangle \\ &= (\lambda/h)^3 \int \exp[i\, P.(r_{1'} - r_1) - (\beta P^2/2m)]\, dP \\ &= \exp[-(\pi/\lambda^2)(r_{1'} - r_1)^2] \end{aligned} \tag{10.1.15}$$

Hence

$$U_1^{S/A}(1) = W_1^{S/A}(1) = 1 \tag{10.1.16}$$

Cluster function for Boltzmann system

We consider a quantum mechanical system (without quantum statistics) obeying Boltzmann statistics. In such a case, the particles are supposed to be distinguishable, and the system is described by the unsymmetrized wave functions; the partition function Q_N will be given by

$$Q_N = (1/N!) \int \ldots \int \sum_x \psi_n^*(1,2,\ldots,N) \exp(-\beta \hat{H}_N)\, \psi_n(1,2,\ldots,N) \prod_{i=1}^{N} d\mathbf{r}_i \qquad (10.1.17)$$

where a factor (1/N!) is introduced in accordance with the rule of correct Boltzmann counting (in view of the supposed distinguishability of the particles). The corresponding probability density matrix is defined as

$$W_N(1',\ldots,N';1,\ldots,N) = \lambda^{3N} \sum_N \psi_n^*(1',\ldots,N') \exp(-\beta \hat{H}_N)\, \psi_n(1,2,\ldots,N) \qquad (10.1.18)$$

and whence the Slater sum is

$$W_N(1,2,\ldots,N) = \lambda^{3N} \sum_n \psi_n^*(1,\ldots,N) \exp(-\beta \hat{H}_N)\, \psi_n(1,\ldots,N) \qquad (10.1.19)$$

However, the expression for the partition function remains the same.

$$Q_N = (1/N!\lambda^{3N}) \int \ldots \int W_N(1,2,\ldots,N) \prod_{i=1}^{N} d\mathbf{r}_i$$

$$= (1/N!\lambda^{3N})\, \mathrm{tr}\,(\exp((-\beta \hat{H}_N)) \qquad (10.1.20)$$

We have defined W_N similar to $W_N^{S/A}$. A simple difference between W_N and $W_N^{S/A}$ is that the statistics (Bose-Einstein or Fermi-Dirac) is not taken into account in defining W_N. If we compare the expressions of $W_N^{S/A}$ and W_N, we find that the functions ψ_x of Eq.(10.1.3) are duly symmetrized whereas the functions ψ_n of Eq.(10.1.19) are not.

We express the function W_N in terms of the cluster function U_l just as $W_N^{S/A}$ is expressed in terms of $U_N^{S/A}$. Thus, we define U_l as

$$W_1(1';1) = W_1^{S/A}(1';1) \qquad (10.1.21a)$$

$$W_2(1',2';1,2) = U_1(1';1)\, U_2(2';2) + U_2(1',2';1,2) \qquad (10.1.21b)$$

$$W_3(1',2',3';1,2,3) = U_1(1';1)\, U_1(2';2)\, U_1(3';3) + U_1(1';1)\, U_2(2',3';2,3) + U_1(2';2)\, U_2(1',3';1,3)$$
$$+ U_1(3';3)\, U_2(1',2';1,2) + U_3(1',2',3';1,2,3) \qquad (10.1.21c)$$

and so on. The function U_l, thus defined, involves only the effect of interaction.

Expansion of $U_l^{S/A}$ in terms of U_l

The function $U_l^{S/A}$ involves both the effects of interaction and statistics. Lee and Yang proposed the method of separating out these two effects. This is done in following ways. The $U^{S/A}$ functions of a physical system are expressed in terms of the U-function of a quantum mechanical system obeying Maxewell-Boltzmann statistics. This expansion is assumed to take care of the statistics of the physical system. Then the U-functions of the Boltzmann system are solved.

From the definitions of $W_N^{S/A}$ and W_N, it is clear that $W_N^{S/A}$ can be expressed in terms of W_N

$$W_N^S(1', \ldots, N'; 1, \ldots, N) = \sum_P W_N(1', \ldots, N'; 1, \ldots, N) \tag{10.1.22}$$

$$W_N^A(1', \ldots, N'; 1, \ldots, N) = \sum_P \delta_P W_N(1', \ldots, N'; 1, \ldots, N) \tag{10.1.23}$$

where

$$\delta_P = +1 \quad \text{if P is even}$$

$$= -1 \quad \text{if P is odd}$$

and P is a permutation of $\{1', \ldots, N'\}$. From (10.1.22) and (10.1.23), we obtain

$$W_1^{S/A}(1',1) = W_1(1',1) \tag{10.1.24a}$$

$$W_2^{S/A}(1',2';1,2) = W_2(1',2';1,2) \pm W_2(2',1';1,2) \tag{10.1.24b}$$

$$W_3^{S/A}(1',2',3';1,2,3) = W_3(1',2',3';1,2,3) \pm W_3(2',1',3';1,2,3) + W_3(2',3',1';1,2,3)$$
$$\pm W_3(1',3',2';1,2,3) + W_3(3',1',2';1,2,3) \pm W_3(3',2',1';1,2,3) \tag{10.1.24c}$$

and so on. With the help (10.1.14) and (10.1.24), we get

$$U_1^{S/A}(1',1) = U_1(1',1) \tag{10.1.25a}$$

$$U_2^{S/A}(1',2';1,2) = U_2(1',2';1,2) \pm U_2(2',1';1,2) + U_1(2';1)\,U_1(1';2) \tag{10.1.25b}$$

and so on.

10.2. Virial Expansion of the Equation of State

In this section, we derive the virial expansion of the equation of state of the quantum system.

We define the l-particle cluster integral $b_l^{S/A}$ by the relation

$$b_l^{S/A} = (1/l!V) \int U_l^{S/A}(1, 2, \ldots, l) \prod_{i=1}^{l} d\mathbf{r}_i \tag{10.2.1}$$

which is the quantum mechanical analogue of the classical cluster integral b_l(see Eq.9.2.9). The first few cluster integral are

$$b_1^{S/A} = (1/V) \int d\mathbf{r}_1 = 1 \tag{10.2.2a}$$

$$b_2^{S/A} = (1/2!V) \int U_2^{S/A}(1,2)\, d\mathbf{r}_1\, d\mathbf{r}_2$$

$$= (1/2) \int U_2^{S/A}(1,2)\, d\mathbf{r}_2 \tag{10.2.2b}$$

$$b_3^{S/A} = (1/3!V) \int U_3^{S/A}(1,2,3)\, d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3$$

$$= (1/6) \int U_3^{S/A}(1,2,3)\, d\mathbf{r}_2\, d\mathbf{r}_3 \qquad (10.2.2c)$$

and so on. Starting from (10.1.5) and (10.1.12), one can obtain an expression for the partition function as

$$Q_N = (1/\lambda^{3N}) \sum_{(m_l)} [\prod_l (V b_l^{S/A})^{m_l}/m_l!] \qquad (10.2.3)$$

Using the relation

$$\Xi = \sum_{N\geq 0} (z^N Z_N/N!) = \sum_{N\geq 0} z^N \lambda^{3N} Q_N \qquad (10.2.4)$$

the grand partition function is given by

$$\Xi = \prod_i [\sum_{(m_l)} (V b_l^{S/A} z^l)^{m_l}/m_l!] = \prod_i [\exp (V b_l^{S/A} z^l)] = \exp [\sum_l V b_l^{S/A} z^l] \qquad (10.2.5)$$

Hence the pressure P and the density ρ of the system are given by

$$\beta P = \lim_{V\to\infty} V^{-1} \ln \Xi = \sum_l b_l^{S/A} z^l \qquad (10.2.6)$$

$$\rho = z\,(\partial/\partial z)\,[V^{-1} \ln \Xi] = \sum_l l b_l^{S/A} z^l \qquad (10.2.7)$$

These are formally identical to equations (9.2.21) and (9.2.22). By eliminating z from these equations, P can be expressed as a function of ρ. Thus, we obtain the expansion of equation of state in the virial form as

$$\beta P = \rho + \sum_{N\geq 0} B_n^{S/A} \rho^n \qquad (10.2.8)$$

where $B_n^{S/A}$ is the nth virial coefficient of the quantum system. They are expressed as

$$B_2^{S/A} = -b_2^{S/A} \qquad (10.2.9)$$

$$B_3^{S/A} = 4(b_2^{S/A})^2 - 2b_3^{S/A} \qquad (10.2.10)$$

$$B_4^{S/A} = -20(b_2^{S/A})^3 - 18 b_2^{S/A} b_3^{S/A} - 3 b_4^{S/A} \qquad (10.2.11)$$

and so on.

We now consider the ideal quantum gas of bosons and fermions. When the interparticle interactions are absent, b_l with $l\geq 2$ vanish for classical gas. This is not true in quantum case.

From Eqs.(6.12.16) and (6.12.19), we get

$$\ln \Xi = (\mp) \sum_i \ln [1 \mp z'^l \exp(-\epsilon_i/kT)]$$

$$= \sum_i \sum_{l\geq 1} ((\pm)^{l-1}/l)\, z'^l \exp(-l\epsilon_i/kT) \tag{10.2.12}$$

where

$$z' = e^{\mu/kT} = \lambda^3 z \tag{10.2.13}$$

and ϵ_i is the energy of the ith particle

$$\epsilon_i = (p_i^2/2m) \tag{10.2.14}$$

Interchanging the summation, Eq.(10.2.12) can be written as

$$\ln \Xi = \sum_{l\geq 1} ((\pm)^{l-1}/l)\, z^l a_l \tag{10.2.15}$$

where a_l is evaluated to be

$$a_l = \lambda^{3l} \sum_i \exp(-l\epsilon_i/kT) = \lambda^{3l} \sum_i \exp(-lp_i^2/2mkT)$$

$$= \lambda^{3l} (4\pi V/h^3) \int_0^\infty \exp(-lp_i^2/2mkT)\, p_i^2\, dp_i$$

$$= \lambda^{3(l-1)} V / l^{3/2} \tag{10.2.16}$$

Substituting the value of a_l in (10.2.15) we obtain an expression for the equation of state of the ideal quantum gas:

$$\beta P^{id} = V^{-1} \ln \Xi = \sum_{l\geq 1} ((\pm)^{l-1}/l^{5/2})\, \lambda^{3(l-1)} z^l \tag{10.2.17}$$

which gives

$$b_l^{id} = ((\pm)^{l-1}/l^{5/2})\, \lambda^{3(l-1)} \tag{10.2.18}$$

where the plus and minus signs refer to the Bose-Einstein and Fermi-Dirac gas respectively. This leads to the following expressions for the virial coefficients of the ideal quantum gas:

$$[B_2^{S/A}]_{id} = \pm(1/4\sqrt{2})\lambda^3 \tag{10.2.19}$$

$$[B_3^{S/A}]_{id} = ((1/8) - (2/9\sqrt{3}))\lambda^6 \tag{10.2.20}$$

$$[B_4^{S/A}]_{id} = \pm [(1/2\sqrt{6}) - (20/6561\sqrt{3}) - (3/32)]\lambda^9 \tag{10.2.21}$$

and so on. In this case, the non-zero values of b_l^{id} arise only from the statistical correlation among the particles.

10.3. Second Virial Coefficient at Low Temperature

We consider a two-body system, which enables us to calculate the second virial coefficient of a quantum mechanical system. For simplicity, we ignore the spin of the particles and assume that the two-body system has no bound states.

From (10.1.24b), the two-body Slater sum, which is also known as the density independent part of pair distribution function, is written as

$$W_2^{S/A}(\mathbf{r}_1,\mathbf{r}_2) = W_2^{dir}(\mathbf{r}_1,\mathbf{r}_2) + W_2^{Exch}(\mathbf{r}_1,\mathbf{r}_2) \tag{10.3.1}$$

where W_2^{dir} and W_2^{Exch} are, respectively, direct and exchange parts of the two-body Slater sum and defined as

$$W_2^{dir}(\mathbf{r}_1,\mathbf{r}_2) \equiv W_2(\mathbf{r}_1,\mathbf{r}_2) = \lambda^6 \sum_x \psi_x^*(\mathbf{r}_1,\mathbf{r}_2) \exp(-\beta \hat{H}_2)\, \psi_x(\mathbf{r}_1,\mathbf{r}_2)$$

$$= \lambda^6 \langle \mathbf{r}_1,\mathbf{r}_2 | \exp(-\beta \hat{H}_2) | \mathbf{r}_1,\mathbf{r}_2 \rangle \tag{10.3.2}$$

$$W_2^{Exch}(\mathbf{r}_1,\mathbf{r}_2) \equiv \pm W_2(\mathbf{r}_2,\mathbf{r}_1) = \pm \lambda^6 \sum_x \psi_x^*(\mathbf{r}_2,\mathbf{r}_1) \exp(-\beta \hat{H}_2)\, \psi_x(\mathbf{r}_1,\mathbf{r}_2)$$

$$= \pm \lambda^6 \langle \mathbf{r}_2,\mathbf{r}_1 | \exp(-\beta \hat{H}_2) | \mathbf{r}_1,\mathbf{r}_2 \rangle \tag{10.3.3}$$

where $\hat{H}_2$ is the Hamiltonian operator for the two-body system, given by

$$\hat{H}_2 = -(\hbar^2/2m)(\nabla_1^2 + \nabla_2^2) + u(|\mathbf{r}_1 - \mathbf{r}_2|) \tag{10.3.4}$$

and $\psi_x(\mathbf{r}_1,\mathbf{r}_2)$ is its eigenfunction with eigenvalues E_x. The Schrodinger equation for the system is

$$[-(\hbar^2/2m)(\nabla_1^2 + \nabla_2^2) + u(|\mathbf{r}_1 - \mathbf{r}_2|)]\, \psi_x = E_x \psi_x \tag{10.3.5}$$

We introduce the centre of mass and relative coordinates

$$\mathbf{R} = (\mathbf{r}_1 - \mathbf{r}_2)/2$$

$$\mathbf{r} = (\mathbf{r}_1 - \mathbf{r}_2)$$

then

$$\hat{H}_2 = \hat{H}_{cm} + \hat{H}_{rel} \tag{10.3.6}$$

where

$$\hat{H}_{cm} = (\hbar^2/4m)\nabla_R^2 \tag{10.3.7a}$$

$$\hat{H}_{rel} = (\hbar^2/m)\nabla_r^2 + u(r) \tag{10.3.7b}$$

and

$$\psi_x(\mathbf{r}_1,\mathbf{r}_2) = \phi_P(R)\, \psi_n(r) = [(1/V^{1/2}) \exp(i\mathbf{P}.\mathbf{R})]\, \psi_n(r) \tag{10.3.8}$$

with

$$E_x = (P^2/4m) + E_n \tag{10.3.9}$$

The wave equation for these motions will be

$$[-(\hbar^2/m)\nabla_r^2 + u(r)]\psi_n(r) = E_n \psi_n(r) \tag{10.3.10}$$

$$-(\hbar^2/4m)\nabla_R^2 \phi_P(R) = (P^2/4m)\phi_P(R) \tag{10.3.11}$$

where E_n and $P^2/4m$ are the energies of relative and centre of mass motion, respectively. The wave function Ψ_n of the relative motion obeys the normalisation condition

$$\int |\Psi_n(r)|^2 \, dr = 1 \tag{10.3.12}$$

Using the centre of mass and relative coordinates, we write (10.3.2) as

$$W_2^{dir}(\mathbf{r}_1,\mathbf{r}_2) = \lambda^6 < \mathbf{R} | \exp(-\beta \hat{H}_{cm}) | \mathbf{R} > < \mathbf{r} | \exp(-\beta \hat{H}_{rel}) | \mathbf{r} > \tag{10.3.13}$$

In the limit $V \to \infty$, the summation over P can be transferred to integration. Thus,

$$< \mathbf{R} | \exp(-\beta \hat{H}_{cm}) | \mathbf{R} > = (1/V) \sum_P \exp(-\beta P^2/4m) = (4\pi/h^3) \int_0^\infty \exp(-\beta P^2/4m) P^2 dP$$

$$= 2\sqrt{2}/\lambda^3 \tag{10.3.14}$$

where

$$\lambda = (2\pi\hbar^2\beta/m)^{1/2}$$

is the thermal wavelength. Thus (10.3.13) becomes

$$W_2^{dir}(\mathbf{r}_1,\mathbf{r}_2) = (2\sqrt{2})\lambda^3 < \mathbf{r} | \exp(-\beta \hat{H}_{rel}) | \mathbf{r} > = (2\sqrt{2})\lambda^3 \sum_n |\psi_n(r)|^2 \exp(-\beta E_n) \tag{10.3.15}$$

Similarly, one can write (10.3.3) as

$$W_2^{Exch}(\mathbf{r}_1,\mathbf{r}_2) = \pm (2\sqrt{2})\lambda^3 < -\mathbf{r} | \exp(-\beta \hat{H}_{rel}) | \mathbf{r} >$$

$$= \pm (2\sqrt{2})\lambda^3 \sum_n \psi_n^*(-r) \, \psi_n(r) \exp(-\beta E_n) \tag{10.3.16}$$

The sum in (10.3.15) and (10.3.16) extends over all eigenfunctions of the relative Hamiltonian $\hat{H}_{rel}$ of two particles.

On the similar argument, the Slater sum of two noninteracting particles can be written as

$$W_2^{0,S/A}(\mathbf{r}_1,\mathbf{r}_2) = W_2^{0,dir}(\mathbf{r}_1,\mathbf{r}_2) + W_2^{0,Exch}(\mathbf{r}_1,\mathbf{r}_2) \tag{10.3.17}$$

where

$$W_2^{0,S/A}(\mathbf{r}_1,\mathbf{r}_2) \equiv W_2^0(\mathbf{r}_1,\mathbf{r}_2) = (2\sqrt{2})\lambda^3 \sum_n |\psi_n^0|^2 \exp(-\beta E_n^0) \tag{10.3.18}$$

$$W_2^{0,Exch}(\mathbf{r}_1,\mathbf{r}_2) \equiv W_2^0(\mathbf{r}_2,\mathbf{r}_1) = (2\sqrt{2})\lambda^3 \sum_n \psi_n^{0*}(-r)\, \psi_n^0(r) \exp(-\beta E_n^0) \tag{10.3.19}$$

From (10.2.26) and (10.2.9), the second virial coefficient for the interacting system is

$$B_2 \equiv -b_2^{S/A} = -(1/2) \int [W_2^{S/A}(\mathbf{r}_1,\mathbf{r}_2) - 1] d\mathbf{r}_2 \tag{10.3.20}$$

and for noninteracting system,

$$B_2^0 = -b_2^{0,S/A} = -(1/2) \int [W_2^{0,S/A}(\mathbf{r}_1,\mathbf{r}_2) - 1] d\mathbf{r}_2 \tag{10.3.21}$$

from which we get

$$B_2 - B_2^0 = -(1/2) \int [W_2^{S/A}(\mathbf{r}_1,\mathbf{r}_2) - W_2^{0,S/A}(\mathbf{r}_1,\mathbf{r}_2)] d\mathbf{r}_2 \tag{10.3.22}$$

where

$$B_2^0 = -(1/4\sqrt{2})\lambda^3 \qquad \text{(ideal Bose gas)}$$

$$= +(1/4\sqrt{2})\lambda^3 \qquad \text{(ideal Fermi gas)} \tag{10.3.23}$$

which arise only from the statistics.

Substituting (10.3.1) and (10.3.17), (10.3.22) can be written as

$$B_2 = B_{dir} + B_{Exch} \tag{10.3.24}$$

where

$$B_{dir} = (-1/2) \int [W_2^{dir}(\mathbf{r}_1,\mathbf{r}_2) - W_2^{0,dir}(\mathbf{r}_1,\mathbf{r}_2)] d\mathbf{r}_2 \tag{10.3.25}$$

$$B_{Exch} = B_2^0 - (1/2) \int [W_2^{Exch}(\mathbf{r}_1,\mathbf{r}_2) - W_2^{0,Exch}(\mathbf{r}_1,\mathbf{r}_2)] d\mathbf{r}_2 \tag{10.3.26}$$

In order to calculate he second virial coefficient, one has to find out the wave function ψ_n and energy values E_n. We follow the method of Uhlenbeck and Bethe (1936, 1937) to calculate the second virial coefficient of a quantum gas.

We first consider the wave functions $\psi_n(r)$ and $\psi_n^0(r)$ for these systems. Since the pair potential u(r) is assumed to be central, these functions can be written as

$$\psi_n(r) \equiv \psi_{klm}(r,\theta,\varphi) = A_{klm} R_{kl}(r)\, Y_{lm}(\theta,\varphi) \tag{10.3.27}$$

$$\psi_n^0(r) \equiv \psi_{klm}^0(r,\theta,\varphi) = A_{klm}^0\, R_{kl}^0(r)\, Y_{lm}(\theta,\varphi) \tag{10.3.28}$$

where R_{kl} and Y_{lm} are, respectively, the radial wave function and the spherical harmonics for the relative motion. For the spherical harmonics.

$$\sum_{l} | Y_{lm}(\theta,\varphi) |^2 = (\pm)^l ((2l+1)/4\pi) \tag{10.3.29}$$

and for the radial function, the boundary condition is

$$R_{kl}(r_0) = R^0_{kl}(r_0) = 0 \tag{10.3.30}$$

where r_0 is a very large value of r which ultimately tends to infinity.

Our next step is to consider the energy values E_n and E^0_n of these two systems. For the noninteracting system, the energy is a continuum and expressed as

$$E^0_n = \hbar^2 k^2/m \tag{10.3.31}$$

where k is the relative wave number. In the case of interacting systems, the energy spectrum E_n contains a set of discrete eigenvalues $\in_B$, corresponding to the two-body bound states, along with a continuum.

$$E_n = \in_B + (\hbar^2 k^2/m) \tag{10.3.32}$$

However, in our discussion we are concerned with continuum state only.

In terms of the wave function ψ_{klm}, the Slater sums are written as

$$W_2^{dir}(\mathbf{r}_1,\mathbf{r}_2) = (2\sqrt{2})\lambda^3 \int_0^\infty dk \sum_{l,m} |\psi_{klm}(r,\theta,\varphi)|^2 \exp(-\beta\hbar^2 k^2/m) = \sum_{l=0}^\infty (2l+1) g_l(r) \tag{10.3.33}$$

$$W_2^{Exch}(\mathbf{r}_1,\mathbf{r}_2) = \pm(2\sqrt{2})\lambda^3 \int dk \sum_{l,m} \psi^*_{klm}(r,\theta,\varphi)\, \psi_{klm}(r,\pi-\theta,\pi+\varphi) \exp(-\beta\hbar^2 k/m)$$

$$= \pm \sum_{l=0}^\infty (-1)^l (2l+1) g_l(r) \tag{10.3.34}$$

where

$$g_l(r) = (\lambda^3/\sqrt{2}\pi) \int_0^\infty dk \exp(-\beta\hbar^2 k^2/m) |R_{kl(r)}|^2 \tag{10.3.35}$$

and

$$W_2^{0,dir}(\mathbf{r}_1,\mathbf{r}_2) = \sum_{l=0}^\infty (2l+1)\, g^0_l(r) \tag{10.3.36}$$

$$W_2^{0,Exch}(\mathbf{r}_1,\mathbf{r}_2) = \pm \sum_{l=0}^\infty (-1)^l (2l+1)\, g^0_l(r) \tag{10.3.37}$$

where

$$g^0_l(r) = (\lambda^3/\sqrt{2}\pi) \int_0^\infty dk \exp(-\beta\hbar^2 k^2/m) |R^0_{kl}(r)|^2 \tag{10.3.38}$$

Then Eqs.(10.3.25) and (10.3.26) can be written as

$$B_{dir} = \sum_{l=0}^\infty (2l+1)\, B_l \tag{10.3.39}$$

$$B_{Exch} = \mp(1/4\sqrt{2})\lambda^3 \pm \sum_{l=0}^{\infty} (-1)^l (2l+1)\, B_l \qquad (10.3.40)$$

where

$$B_l = (\sqrt{2})\lambda^3 \int_0^{\infty} dk \exp(-\lambda^2 k^2/2\pi)\, A_{kl} \qquad (10.3.41)$$

$$A_{kl} = \int_0^{\infty} dr\, r^2 [\, | R^0_{kl}(r) |^2 - | R_{kl}(r) |^2] \qquad (10.3.42)$$

This, in principle, is calculable for any given potential u(r) through the radial wave function $R_{kl}(r)$ and $R^0_{kl}(r)$.

In (10.3.42), $R^0_{kl}(r)$ is the radial wave function for free particle (u(r) = 0), given

$$R^0_{kl}(r) = (1/r)(\pi kr/2)^{1/2} j_{l+1/2}(kr) \qquad (10.3.43)$$

and R_{kl} is the radial wave function for a gas whose molecules interact via a central potential. If the central potential is a hard sphere potential.

$$u(r) = \infty \qquad r < d$$

$$= 0 \qquad r > d \qquad (10.3.44)$$

d being the hard sphere diameter, then the function R_{kl} is given by

$$R_{kl}(r) = 0 \qquad r < d$$

$$= (1/r)(\pi kr/2)^{1/2} ([j_{l+1/2}(kr)\, \eta_{l+1/2}(kd) - j_{l+1/2}(kd)\, \eta_{l+1/2}(kr)]/[j^2_{l+1/2}(kd) + \eta^2_{l+1/2}(kd)]^{1/2})$$

$$r > d \qquad (10.3.45)$$

where the functions $j_{l+1/2}(x)$ and $\eta_{l+1/2}(x)$ are respectively the spherical Bessel functions and the spherical Neumann functions;

$$j_{1/2}(X) = (2X/\pi)^{1/2} (\sin X/X)$$

$$j_{3/2}(X) = (2X/\pi)^{1/2} [(\sin X - X\cos X)/X^2]$$

$$j_{5/2}(X) = (2X/\pi)^{1/2} [((3-X^2)\sin X - 3X\cos X)/X^2]$$

and

$$\eta_{1/2}(X) = -(2X/\pi)^{1/2} (X\cos X/X)$$

$$\eta_{3/2}(X) = -(2X/\pi)^{1/2} [(X\sin X + \cos X)/X^2]$$

$$\eta_{5/2}(X) = (2X/\pi)^{1/2} [((3X\sin X + (3-X^2)\cos X)/X^2]$$

Then (10.3.42) is written as

$$A_{kl} = (\pi k/2) \int_0^\infty dr\, r\, [j^2_{l+1/2}(kr) - ((j_{l+1/2}(kr)\, \eta_{l+1/2}(kd) - j_{l+1/2}(kd)\, \eta_{l+1/2}(kr))^2 / (j^2_{l+1/2}(kd)+\eta^2_{l+1/2}(kd))] \quad (10.3.46)$$

Using the properties of Bessel functions, this integral can be evaluated to give

$$A_{kl} = (2/\pi^2 k)\, [j^2_{l+1/2}(kd) + \eta^2_{l+1/2}(kd)]^{-1} \quad (10.3.47)$$

and hence

$$B_l = (2\sqrt{2}\lambda^3/\pi^2) \int_0^\infty (dk/k)\, [j^2_{l+1/2}(kd) + \eta^2_{l+1/2}(kd)]^{-1} \exp(-\lambda^2 k^2/2\pi)$$

$$= (8/\sqrt{\pi}) d^3 \Lambda^3 \int_0^\infty (dX/X)\, [j^2_{l+1/2}(X) + \eta^2_{l+1/2}(X)]^{-1} \exp(-\Lambda^2 X^2) \quad (10.3.48)$$

where $\Lambda = (\lambda/d)/(2\pi)^{1/2}$, from which one can calculate B_l for different values of l. Substituting these values in (10.3.39) and (10.3.40), we obtain expresseions for B_{dir} and B_{Exch}.

$$B_{dir} = d^3(\lambda/d)^2\, [1 + 3\pi\, (d/\lambda)^2 - (22\pi^2/3)\, (d/\lambda)^4 + (191\pi^3/3)(d/\lambda)^6 + \ldots] \quad (10.3.49)$$

$$B_{Exch} = \mp\, (d^3/2^{5/2})(\lambda/d)^3\, [1 - 4\sqrt{2}(d/\lambda) + 12\sqrt{2}\pi\, (d/\lambda)^3 - (128\sqrt{2}\pi^2/3)\, (d/\lambda)^5 + \ldots] \quad (10.3.50)$$

Finally the second virial coefficient of a gas at low temperature is obtained from (10.3.24)

$$B_2/B_2^c = -(3/2^{7/2}\pi)\, (\lambda/d)^3\, [1 - 8\sqrt{2}(d/\lambda) + (40\sqrt{2}\pi^2/3)\, (d/\lambda)^5 \ldots] \quad \text{(boson)} \quad (10.3.51)$$

$$= (3/2^{7/2}\pi)\, (\lambda/d)^3\, [1 + 24\sqrt{2}\pi\, (d/\lambda)^3 - 72\sqrt{2}\pi^2\, (d/\lambda)^5 \ldots] \quad \text{(fermion)} \quad (10.3.52)$$

where $B_2^c = 2\pi d^3/3$ is the second virial coefficient of the classical hard sphere gas.

10.4. Expansion of the Slater Sum at high Temperature

The theory described in the previous section is not suitable for high temperature as it gives a series in powers of (d/λ). At high temperature, where the quantum effects are small and treated as a correction to the classical value, the usual method is to expand the properties of the system about the classical value in ascending power of Planck's constant $\hbar$. Further at high temperature the exchange effect is assume to be negligible and the Slater Sum arises only due to the direct part. Thus in this case $W_N \equiv W_N^{dir}$.

10.4.1. Cluster expansion

At moderately high temperature, when the deviation from the classical behaviour is small, we can write

$$W_N = W_N^c W_N^m \tag{10.4.1}$$

where W_N^c is the Boltzmann factor, given by

$$W_N^c(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \exp\left[-\beta \sum_{i<j} u(\mathbf{r}_i, \mathbf{r}_j)\right] \tag{10.4.2}$$

and W_N^m is a function, which measures the deviation from the classical. If the pair potential has a hard core, both W_N^c and W_N vanish for particle configuration in which hard cores overlap. In this case W_N^m can be taken as zero also.

We now express W_N^m in terms of the 'modified' Ursell function U_l^m. Thus

$$W_1^m(\mathbf{r}_1) = U_1^m(\mathbf{r}_1) = 1 \tag{10.4.3a}$$

$$W_2^m(\mathbf{r}_1, \mathbf{r}_2) = 1 + U_2^m(\mathbf{r}_1, \mathbf{r}_2) \tag{10.4.3b}$$

$$W_3^m(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = 1 + U_2^m(\mathbf{r}_1, \mathbf{r}_2) + U_2^m(\mathbf{r}_1, \mathbf{r}_3) + U_2^m(\mathbf{r}_2, \mathbf{r}_3) + U_3^m(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \tag{10.4.3c}$$

$$\vdots$$

$$W_N^m(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = 1 + \Sigma U_2^m(\mathbf{r}_i, \mathbf{r}_j) + \Sigma U_2^m(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) + \ldots \tag{10.4.3d}$$

The above equation can be solved successively for U_2^m, U_3^m, ...

$$U_2^m(\mathbf{r}_1, \mathbf{r}_2) = W_2^m(\mathbf{r}_1, \mathbf{r}_2) - 1 \tag{10.4.4a}$$

$$U_3^m(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = W_3^m(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) - W_2^m(\mathbf{r}_1, \mathbf{r}_2) - W_2^m(\mathbf{r}_1, \mathbf{r}_3) - W_2^m(\mathbf{r}_2, \mathbf{r}_3) + 2 \tag{10.4.4b}$$

From (9.4.1) and (9.4.3d), we obtain an expression for W_N

$$W_N(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = W_N^c(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)\ [1 + \Sigma U_2^m(\mathbf{r}_i, \mathbf{r}_j) + \Sigma U_3^m(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) + \ldots\ ] \tag{10.4.5}$$

The U_l^m appearing in (9.5.4) can, in principle, be found from the solution of the quantum mechanical l-body problem. Unfortunately, the actual calculation is too involved to be feasible. It is only for hard sphere system that U_2^m has been evaluated.

Evaluation of U_2^m for the hard sphere system

For hard sphere U_2^m becomes identical to the Ursell function U_2. From (10.4.4a), we have

$$U_2(r) = W_2(r) - 1 \tag{10.4.6}$$

where $W_2(r)$ is the two-body Slater sum. At high temperature it is defined by (10.3.15) i.e.

$$W_2(r) \equiv W_2^{dir}(r) = (2\sqrt{2})\lambda^3 \langle \mathbf{r} | \exp(-\beta \hat{H}_{rel}) | \mathbf{r} \rangle$$

$$= (2\sqrt{2})\lambda^3 \Sigma_n \psi_n^*(r) \exp(-\beta \hat{H}_{rel})\, \psi_n(r) \tag{10.4.7}$$

In order to calculate $U_2(r)$, we follow the method of Uhlenbeck and Bethe (1936) and replace the hard sphere by a hard wall at r = d and take the wave function.

$$\psi(r) = 0 \qquad r < d$$

$$= (1/\pi^{1/2}) \sinh(r-d) \qquad r > d \tag{10.4.8}$$

where d is the hard sphere diameter. For high temperature, where λ is small compared to d, the curvature effect of the wall may be neglected to first approximation. In this case (10.4.7) can be expressed for r > d as

$$W_2(r) = (\sqrt{2}/\pi) \int_0^\infty dk \exp(-\lambda^2 k^2/2\pi) \sin^2 k(r-d) = 1 - \exp[-(2\pi/\lambda^2)(r-d)^2] \tag{10.4.9}$$

while for r < d, $W_2(r) = 0$

Finally from (10.4.5) and (10.4.7), we obtain the results for $U_2^m(r)$

$$U_2^m(r) = -\exp[-(2\pi/\lambda^2)(r-d)^2] + 0(\lambda^2), \quad r > d \tag{10.4.10}$$

10.4.2. Perturbation expansion for analytic potential

We now discuss the expansion of the Slater sum in powers of $\hbar$ using a method known as perturbation expansion given by Wigner (1932) and Uhlenbeck and Gropper (1932). In this method, we choose the kinetic energy as a reference system.

We write Hamiltonian $\hat{H}$ as

$$\hat{H} = \hat{H}_0 + U \tag{10.4.11a}$$

where

$$\hat{H}_0 = -(\hbar^2/2m) \sum_{i=0}^{N} \nabla_i^2 \tag{10.4.11b}$$

is the kinetic energy operator, treated as the reference, and the interaction potential U is taken as the perturbation over the reference system. In this case, we choose the free-particle basis function.

Let ψ_k^0 be the free-particle eigenfunction for the Hamiltonian $\hat{H}_0$, then

$$H_0 \psi_k^0 = E_k^0 \psi_k^0 \tag{10.4.12}$$

where

$$E_k^0 = \hbar^2 K^2/2m = (\hbar^2/2m) \sum_{i=1}^{N} K_i^2 \tag{10.4.13a}$$

and

$$\psi_k^0 = (1/V^{N/2}) \exp[i \sum_{i=1}^{N} \mathbf{K}_i . \mathbf{r}_i] \tag{10.4.13b}$$

In terms of the wave functions ψ_k^0, the Slater sum is written as

$$W_N = \lambda^{3N} \sum_k \psi_k^{0*} \exp[-\beta(\hat{H}_0 + U)]\, \psi_k^0 \tag{10.4.14}$$

where

$$\beta = 1/kT.$$

In the limit $V \to \infty$, the summation over $\mathbf{K}_i$ may be replaced by an integration over $\mathbf{K}_i$ according to

$$\sum_{K_i} \to (V/(2\pi)^3) \int d\mathbf{K}_i \tag{10.4.15}$$

Substituting (10.4.13) in (10.4.14) and transforming the summation into integration, we get

$$W_N = (\lambda/2\pi)^{3N} \int\int \exp(-\sum_i \mathbf{K}_i.\mathbf{r}_i) \exp[-\beta(\hat{H}_0 + U)] \exp(i \sum_i \mathbf{K}_i.\mathbf{r}_i) \prod_{i=1}^{N} d\mathbf{K}_i \tag{10.4.16}$$

The wave functions are so normalised that $W_N = 1$ for $U = 0$. We write the integrand as

$$X = \exp(-i \sum_i \mathbf{K}_i.\mathbf{r}_i) \exp[-\beta(\hat{H}_0 + U)] \exp(i \sum_i \mathbf{K}_i.\mathbf{r}_i) \tag{10.4.17}$$

with the condition that $X = 1$ when $\beta = 0$. Differentiating with respect to β, we get

$$\partial X/\partial\beta = -\exp(-i \sum_i \mathbf{K}_i.\mathbf{r}_i)(\hat{H}_0 + U)[\exp(i \sum_i \mathbf{K}_i.\mathbf{r}_i)X]$$

Using (10.4.10) we can obtain the equation for X

$$\partial X/\partial\beta = -EX + (\hbar^2/2m) \sum_i (2i\mathbf{K}_i.\nabla_i X + \nabla_i^2 X) \tag{10.4.18}$$

where

$$E = (\hbar^2/2m) \sum_i K_i^2 + U \tag{10.4.19}$$

is the energy of the system. In the limit $\beta \to 0$, (10.4.18) reduces to

$$\partial X/\partial\beta = -EX$$

which has the solution of the form

$$X = e^{-\beta E}$$

For $\beta > 0$, we assume the solution of (10.4.18) as

$$X = e^{-\beta E}\omega \tag{10.4.20}$$

Then, the differential equation (10.4.19) becomes

$$\partial\omega/\partial\beta = (i\hbar/m) \sum_i [\mathbf{P}_i.\nabla_i\omega - \beta(\mathbf{P}_i.\nabla_i U)\omega] + (\hbar^2/2m) \sum_i [\nabla_i^2\omega - 2\beta\nabla_i\omega.\nabla_i U - \beta\omega\nabla_i^2 U + \beta^2(\nabla_i U)^2] \tag{10.4.21}$$

with the initial condition

$$\lim_{\beta \to 0} \omega = 1$$

Here we have used expression for momentum, $\mathbf{P}_i = \hbar\mathbf{K}_i$. In order to obtain an expansion in powers of $\hbar$, we write

$$\omega = 1 + \sum_{n-1} \hbar^n \omega_n \tag{10.4.22}$$

Substituting this value in (10.4.21) and equating equal power of $\hbar$, we obtain

$$\partial\omega_1/\partial\beta = -(i\beta/m) \sum_i \mathbf{P}_i.\nabla_i U$$

$$\partial\omega_2/\partial\beta = (1/2m) \sum_i [-\beta\nabla_i^2 U + \beta^2(\nabla_i U) + 2i\mathbf{P}_i.\nabla_i\omega_1 - 2i\beta(\mathbf{P}_i.\nabla_i U)\omega_1] \tag{10.4.23}$$

Evaluating these two equations successively we get

$$\omega_1 = -(i\hbar\beta^2/2m) \sum_i \nabla_i U$$

$$\omega_2 = (1/m) \sum_i [-(1/4)\beta^2\nabla_i^2 U + (1/6)\beta^3(\nabla_i U)^2] + (\hbar^2/m^2)[(1/6)\beta^3 \sum_{i,j} (\mathbf{K}_i.\nabla_i)(\mathbf{K}_j.\nabla_j)U$$

$$-(1/8)\beta^4 (\sum_i (\mathbf{K}_i.\nabla_i U)^2] \tag{10.4.24}$$

Similarly, one can evaluate $\omega_3, \omega_4, \ldots$. Thus, the required integrand (10.4.20) is

$$X = \exp[-\beta\{(\hbar^2/2m) \sum_i K_i^2 + U\}][1 + \hbar\omega + \hbar\omega^2 + \ldots] \tag{10.4.25}$$

where ω_1 and ω_2 are given by (10.4.23) and (10.4.24) respectively. Substituting (10.4.25) in (10.4.16) and integrating over $\mathbf{K}_i$, we obtain an expression for W_N

$$W_N = e^{-\beta U}[1 + (\hbar^2\beta^2/12m) \sum_{i=1}^{N} \{-\nabla_i^2 U + (1/2)\beta(\nabla_i U)^2\} + \ldots] \tag{10.4.26}$$

The first term of this series is the Boltzmann factor, and the second term, which is proportional to $\hbar^2$ is the first order quantum correction to it. Equation (10.4.26) can be used to calculate the deviation from the classical behaviour of Boltzmann factor, provided the temperature is sufficiently high so that the higher terms can be neglected.

Substituting (10.4.26) in the expression (4.9.6), the partition function can be written as

$$Q_N = (1/N!\lambda^{3N}) \int\int e^{-\beta U} [1 + (\hbar^2\beta^2/12m) \sum_i \{-\nabla_i^2 U + (1/2)\beta(\nabla_i U)^2\}] \prod_{i=1}^{N} d\mathbf{r}_i \quad (10.4.27)$$

Integrating by parts, it can be shown that

$$\int e^{-\beta U} \nabla_i^2 U \, d\mathbf{r}_i = e^{-\beta U} \nabla_i U + \beta \int e^{-\beta U} (\nabla_i U)^2 \, d\mathbf{r}_i = \beta \int e^{-\beta U} (\nabla_i U)^2 \, d\mathbf{r}_i$$

as the contribution of the first term is neglected. Then (10.4.27) can be expressed in the form

$$Q_N = Q_N^C [1 - (\hbar^2\beta^3/24m) \sum_i <(\nabla_i U)^2>] \quad (10.4.28)$$

where Q_N^C is the classical partition function and $<(\nabla_i U)^2>$ is the mean value defined by

$$<(\nabla_i U)^2> = (Z_N^C)^{-1} \int \ldots \int (\nabla_i U)^2 \exp[-\beta U] \prod_{i=1}^{N} d\mathbf{r}_i \quad (10.4.29)$$

Using the relation

$$A = -kT \ln Q_N$$

the Helmholtz free energy is given by

$$A = A^C + (\hbar^2\beta^2/24m) \sum_i <(\nabla_i U)^2> \quad (10.4.30)$$

where A^C is the classical Helmholtz free energy and the first order correction to it is proportional to $\hbar^2$. It is clear from this expression that the quantum correction to the classical value is always positive and increases with decrease of atomic mass and temperature.

If we substitute (10.4.26) in (10.4.4a) and (10.4.4b) and assume the total potential as the pair wise additive, we obtain

$$U_2^m(\mathbf{r}_1, \mathbf{r}_2) = -(\hbar^2\beta^2/6m) [\nabla^2 u(\mathbf{r}_1, \mathbf{r}_2) - (1/2)\beta(\nabla u(\mathbf{r}_1, \mathbf{r}_2))^2] + 0(\hbar^4) \quad (10.4.31)$$

$$U_3^m(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = (\hbar^2\beta^3/12m) [\nabla_1 u(\mathbf{r}_1, \mathbf{r}_2). \nabla_1 u(\mathbf{r}_1, \mathbf{r}_3) + \nabla_2 u(\mathbf{r}_1, \mathbf{r}_2). \nabla_2 u(\mathbf{r}_2, \mathbf{r}_3) + \nabla_3 u(\mathbf{r}_1, \mathbf{r}_3). \nabla_3 u(\mathbf{r}_2, \mathbf{r}_3)] + 0(\hbar^4) \quad (10.4.32)$$

Thus the contribution of the first order of $\hbar^2$ comes from both U_2^m and U_3^m. Eq.(10.4.26) can be expressed in the form of (10.4.5).

10.5. Second Virial Coefficient at High Temperature

At high temperature, the second virial coefficient is given by [see Eq.(10.3.20)]

$$B_2 = B_{dir} = -2\pi \int_0^\infty [W_2^{dir}(r) - 1] = -2\pi \int_0^\infty [W_2(r) - 1] \quad (10.5.1)$$

where $W_2(r)$ is the two-body Slater sum. At high temperature, where the quantum effect is small, we can write $W_2(r)$ as

$$W_2(r) = \exp(-\beta u(r)) [1 + U_2^m(r)] \tag{10.5.2}$$

Substituting (10.5.2) in (10.5.1), we obtain an expression for the second virial coefficient B_2 as

$$B_2 = B_2^c + B_2^{qc} \tag{10.5.3}$$

where B_2^c and B_2^{qc} are the classical and quantum correction values of B_2, respectively. They are expressed as

$$B_2^c = -2\pi \int_0^\infty [\exp(-\beta u(r)) - 1] r^2 \, dr \tag{10.5.4}$$

$$B_2^{qc} = -2\pi \int_0^\infty \exp(-\beta u(r)) U_2^m(r) r^2 \, dr \tag{10.5.5}$$

These are the general expressions valid for any central potential. Below, we give the results for B_2 for some specific potential models, for example, the hard spheres and Lennard-Jones (12-6) potential.

Hard sphere model

We first consider the hard sphere model [Eq.(9.4.9)]. For this potential,

$$B_2^c = 2\pi d^3/3 \tag{10.5.6}$$

and $U_2^m(r)$ is given by (10.4.18).

Substituting this value of U_2^m in (10.5.5), we obtain the quantum correction to the second virial coefficient as

$$B_2^{qc} = 2\pi \int_d^\infty \exp[(-2\pi/\lambda^2)(r - d)^2] r^2 \, dr = (2\pi d^3/2\sqrt{2})(\lambda/d) + 0(\lambda/d)^2 \tag{10.5.7}$$

and the second virial coefficient for the hard sphere model as

$$B_2 = B_2^c [1 + (3/2\sqrt{2})(\lambda/d) + 0(\lambda/d)^2] \tag{10.5.8}$$

where the first term is the classical value of B_2 and the second term is the first order quantum correction to it. The quantum corrections up to the seventh order have been estimated for the hard sphere gas. These are discussed at length in a review article by Singh and Sinha (1981).

Lennard-Jones (12-6) model

Substituting (10.4.31) in (10.5.5), and integrating by parts, we get

$$B_2^{qc} = (\hbar^2/m) B_2^1 \tag{10.5.9}$$

where

$$B_2^I = 2\pi(\beta^3/12) \int_0^\infty \exp[-\beta u(r)] (\partial u(r)/\partial r)^2 r^2 dr \qquad (10.5.10)$$

Thus, the first order quantum correction to the second virial coefficient for an analytic potential is of the order of $(\hbar^2)$, and not $\hbar$ which we obtain for the hard system.

For evaluation of the quantum correction to the second virial coefficient, we represent the pair potential by the Lennard-Jones (12-6) model [Eq.(9.4.11)] for which the expression for B_2^c is given in Sec.9.5.

After integrating by parts, (10.5.10) can be rewritten as

$$B_2^I = 2\pi(\beta^2/12) \int_0^\infty \exp[-\beta u(r)] (\partial/\partial r) [u(r) r^2] dr \qquad (10.5.11)$$

Substituting (9.4.11) and using the reduced quantities $r^* = r/\sigma$ and $T^* = kT/\epsilon \equiv (\beta\epsilon)^{-1}$ (10.5.11) can be written as

$$B_2^I = (2\pi\sigma^3/3) (1/4T^*\epsilon) [-11P(T^*) + 36Q(T^*)] \qquad (10.5.12)$$

where

$$P(T^*) = (4/T^*) \int_0^\infty \exp[-(4/T^*)(r^{*-12} - r^{*-6})] [-12r^{*-12} + 6r^{*-6}] dr^* \qquad (10.5.13)$$

$$Q(T^*) = \int_0^\infty \exp[-(4/T^*)(r^{*-12} - r^{*-6})] r^{*-6} dr^* \qquad (10.5.14)$$

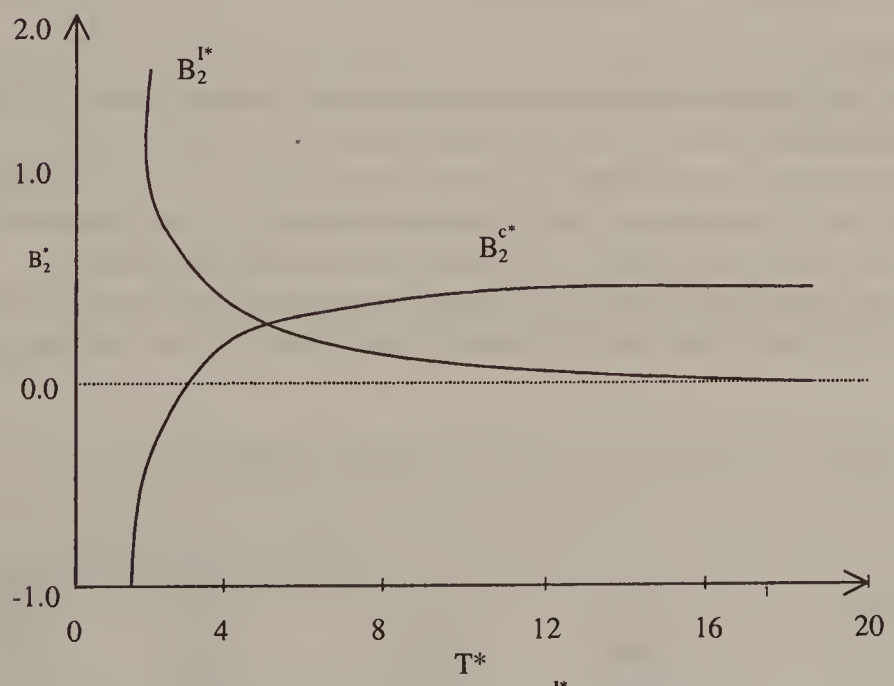


Fig.10.1. The first quantum correction B_2^{I*} for the Lennard-Jones (12-6) gas as a function of T^*.B_2^{c*} is also shown.

The integrals of $P(T^*)$ and $Q(T^*)$ can be evaluated by expanding $\exp[4r^{*-6}/T^*]$ in an infinite series and following the method discussed in Sec.9.5. Thus,

$$B_2^I = (2\pi\sigma^3/3)\,(1/4T^*\epsilon)\,[-(1/12)\sum_{j=0}^{\infty}((11-36i)/i!)2^{6i+1/6}\,\Gamma((6i-1)/12)T^{*-(6i+1)/12}] \qquad (10.5.15)$$

Then, the final result for the reduced second virial coefficient $B_2^* \equiv B_2/(2\pi\sigma^3/3)$ can be obtained from (10.5.3) in the form

$$B_2^* = B_2^{c*} + \Lambda^{*2}\, B_2^{I*} + \ldots \qquad (10.5.16)$$

where

$$B_2^{c*} = T^{*-1/4}\sum_{i=0}^{\infty} b_i\, T^{*-i/2} \qquad (10.5.17)$$

$$B_2^{I*} = T^{*-13/12}\sum_{i=0}^{\infty} b_i^I\, T^{*-i/2} \qquad (10.5.18)$$

and $\Lambda^* = h/\sigma\sqrt{(m\epsilon)}$ is the quantum parameter. The expansion coefficients b_i and b_i^I were given by de Boer and Michel (1938).

$$b_i \equiv -(2^{i+1/2}/4i!)\,\Gamma((2i-1)/4) \qquad (10.5.19)$$

$$b_i^I = -((11-36i)/192\pi^2)\,(2^{i+1/6}/i!)\,\Gamma((6i-1)/12) \qquad (10.5.20)$$

where Γ is the gamma function.

From (10.5.16), we find that the reduced second virial coefficient B_2^* depends not only on T^* but also on the quantum parameter Λ^*.

The first order quantum correction coefficient B_2^{I*} for the Lennard-Jones (12-6) potential is plotted in Fig.10.1. The values for B_2^{c*} are reported in Fig.9.9. We note that while B_2^{c*} first increase and then begins to decrease with decrease of temperature T^*, B_2^{I*} increases rapidly with decrease of T^*.

Results of B_2^* for some gases, such as Ne, D_2, H_2 and He^4 as a function of T^* are shown in Table 10.2. Values of B_2^{c*} are also reported there. We find that the quantum effects increase with the quantum parameter Λ^*.

Table 10.2. Values of the Reduced Second Virial Coefficient B_2^*

T^*	B_2^{c*}	B_2^*			
		Ne	D_2	H_2	He^4
100.00	0.464	0.439	0.356	0.247	-0.053
50.00	0.508	0.490	0.431	0.354	0.140
10.00	0.461	0.523	0.724	0.987	1.715
5.00	0.243	0.417	0.980	1.716	3.755
2.00	-0.627	-0.055	1.810	4.244	10.990

10.6. Quantum Field Theory for Interacting Systems

We consider imperfect gases consisting of N identical molecules, each of mass m at low temperatures.

Let the Hamiltonian of the system be

$$\hat{H} = -(\hbar^2/2m) \sum_{i=1}^{N} \nabla_i^2 + \sum_{i<j} u(\mathbf{r}_i, \mathbf{r}_j) \tag{10.6.1}$$

where $u(\mathbf{r}_i, \mathbf{r}_j)$ is the pair potential between the molecules i and j. In order to investigate the low temperature behaviour of gases, we should rigorously solve the Schrodinger equation for the system

$$\hat{H}\psi = E\psi \tag{10.6.2}$$

But this is impossible as the system is an assembly of roughly 10^{23} particles. In the present section, we present a method of quantum field theory, based on the concept of a quantized field, which is represented by the field operators $\hat{\psi}(\mathbf{r})$ and their Hermitian adjoint $\hat{\psi}^+(\mathbf{r})$. The field operators $\hat{\psi}(\mathbf{r})$ and $\hat{\psi}^+(\mathbf{r})$ are defined for all values of the position coordinate $\mathbf{r}$. These operators operate on a Hilbert space labelled by continuous single particle eigenvalue r. The field operators are assumed to satisfy the following commutation rules:

$$[\hat{\psi}(\mathbf{r}), \hat{\psi}^+(\mathbf{r}')]_\mp = \delta(\mathbf{r} - \mathbf{r}') \tag{10.6.3a}$$

$$[\hat{\psi}(\mathbf{r}), \hat{\psi}(\mathbf{r}')]_\mp = [\hat{\psi}^+(\mathbf{r}), \hat{\psi}^+(\mathbf{r}')]_\mp = 0 \tag{10.6.3b}$$

where $[\hat{A}, \hat{B}]_\mp = \hat{A}\hat{B} \mp \hat{B}\hat{A}$; the minus sign stands for bosons and the plus, for fermions. The commutation relations with the plus sign are usually referred to as the anticommutation relations.

We now introduce the particle-number operator $\hat{N}$ and Hamiltonian operator $\hat{H}$ through the definitions

$$\hat{N} = \int d^3\mathbf{r}\, \hat{\psi}^+(\mathbf{r})\, \psi(\mathbf{r}) \tag{10.6.4}$$

and

$$\hat{H} = -(\hbar^2/2m) \int d^3\mathbf{r}\, \hat{\psi}^+(\mathbf{r})\, \nabla^2 \hat{\psi}(\mathbf{r}) + (1/2) \int d^3\mathbf{r}_1\, d^3\mathbf{r}_2\, \hat{\psi}^+(\mathbf{r}_1)\, \hat{\psi}^+(\mathbf{r}_2)\, u(\mathbf{r}_1, \mathbf{r}_2) \hat{\psi}(\mathbf{r}_1) \hat{\psi}(\mathbf{r}_2) \tag{10.6.5}$$

where $u(\mathbf{r}_1, \mathbf{r}_2)$ is the pair interaction potential. The operator $\hat{\psi}^+(\mathbf{r})\hat{\psi}(\mathbf{r})$ may be interpreted as the number density operator, so that $\hat{N}$ represents the number of particles in the field.

We now expand the field operators $\hat{\psi}(\mathbf{r})$ and $\hat{\psi}^+(\mathbf{r})$ in terms of a complete orthonormal set of single wave function $u_k(\mathbf{r})$. Thus

$$\hat{\psi}(\mathbf{r}) = \sum_k \hat{a}_k u_k(\mathbf{r}) \tag{10.6.6a}$$

$$\hat{\psi}^+(\mathbf{r}) = \sum_k \hat{a}_k^+ u_k^*(\mathbf{r}) \tag{10.6.6b}$$

For simplicity, we can express them in terms of plane waves as

$$\hat{\psi}(\mathbf{r}) = (1/V^{1/2}) \sum_k \hat{a}_k e^{i\mathbf{k}.\mathbf{r}} \tag{10.6.7a}$$

$$\hat{\psi}^+(\mathbf{r}) = (1/V^{1/2}) \sum_k \hat{a}_k^+ e^{-i\mathbf{k}.\mathbf{r}} \tag{10.6.7b}$$

In view of the orthonormality of the wave functions, we have

$$\int d^3\mathbf{r}\, u_k^*(\mathbf{r})\, u_{k'}(\mathbf{r}) = \delta_{kk'} \tag{10.6.8}$$

Equation (10.6.6) can be solved to give

$$\hat{a}_k = \int u_k^*(\mathbf{r})\, \hat{\psi}(\mathbf{r})\, d^3\mathbf{r} \tag{10.6.9a}$$

$$\hat{a}_k^+ = \int u_k(\mathbf{r})\, \hat{\psi}^+(\mathbf{r})\, d^3\mathbf{r} \tag{10.6.9b}$$

The coefficients $\hat{a}_k$ and $\hat{a}_k^+$ are operators which operate on the elements of the relevant Hilbert space. They take over the role of the degree of freedom of the field. In the thermodynamic limit, the sum over the discrete $\mathbf{k}$ is replaced by an integral over $\mathbf{k}$, i.e.

$$(1/V) \sum_k \rightarrow (1/(2\pi)^3) \int d^3\mathbf{k}$$

If we multiply the commutation rules (10.6.3) by $u_k^*(\mathbf{r})\, u_{k'}(\mathbf{r}')$ on both the sides and integrate over $\mathbf{r}$ and $\mathbf{r}'$, we obtain the commutation rules for the operators $\hat{a}_k$ and $\hat{a}_k^+$. Thus

$$[\hat{a}_k, \hat{a}_{k'}^+]_\mp = \delta_{kk'} \tag{10.6.10a}$$

$$[\hat{a}_k, \hat{a}_{k'}]_\mp = [\hat{a}_k^+, \hat{a}_{k'}^+]_\mp = 0 \tag{10.6.10b}$$

In the case of fermions, the operators $\hat{a}_k$ and $\hat{a}_k^+$ possess certain explicit properties, i.e

$$\begin{aligned} \hat{a}_k \hat{a}_k &= 0 \qquad \text{for all } \mathbf{k} \\ \hat{a}_k^+ \hat{a}_k^+ &= 0 \qquad \text{for all } \mathbf{k} \end{aligned} \tag{10.6.11}$$

No such properties are displayed for bosons.

Let us now express the operators $\hat{N}$ and $\hat{H}$ in terms of the operators $\hat{a}_k$ and $\hat{a}_k^+$. Substituting (10.6.6) in (10.6.4), we get

$$\hat{N} \equiv \sum_{k,k'} \hat{a}_k^+ \hat{a}_{k'} \int u_k^*(\mathbf{r})\, u_{k'}(\mathbf{r})\, d^3r = \sum_k \hat{a}_k^+ \hat{a}_k = \sum_k \hat{N}_k \tag{10.6.12}$$

where

$$\hat{N}_k = \hat{a}_k^+ a_k \tag{10.6.13}$$

is the particle-number operator pertaining to the single-particle state $\mathbf{k}$. With the help of the commutation rules for $\hat{a}_k$'s, it can be shown that

$$[\hat{N}_k, \hat{N}_{k'}]_\mp = [\hat{a}_k^+ \hat{a}_k, \hat{a}_{k'}^+ \hat{a}_{k'}]_\mp = \hat{a}_k^+ [\hat{a}_k, \hat{a}_{k'}^+]_\mp \hat{a}_{k'} + \hat{a}_{k'}^+ [\hat{a}_k^+, \hat{a}_{k'}]_\mp \hat{a}_k = 0 \tag{10.6.14}$$

Thus $\hat{N}_k$'s for different states $\mathbf{k}$ commute with each other, so they can be diagonalised simultaneously.

Let a particular member of the basis be represented by $|N_1, N_2, \ldots, N_k \ldots>$, i.e.

$$|\phi_N> = |N_1, N_2, \ldots, N_k \ldots> \tag{10.6.15}$$

and, assuming that it is normalised, we have

$$<\phi_N | \phi_N> = 1 \tag{10.6.16}$$

The vector for which all $\hat{N}_{k'} = 0$ will be called the ground state (or vacuum state)

$$|\phi_N> = |0, 0, \ldots 0> \equiv |0> \tag{10.6.17}$$

We can interpret $\hat{a}_k$ as an annihilation operator for a particle in the state $\mathbf{k}$ while $\hat{a}_k^+$ can be interpreted as a creation operator for the state $\mathbf{k}$. Thus

$$\hat{a}_k |N_1, N_2, \ldots, N_k \ldots> = \sqrt{N_k}\, |N_1, N_2, \ldots, N_k - 1, \ldots> \tag{10.6.18}$$

$$\hat{a}_k^+ |N_1, N_2, \ldots, N_k \ldots> = \sqrt{(N_k + 1)}\, |N_1, N_2, \ldots, N_k + 1, \ldots> \tag{10.6.19}$$

The operator $\hat{N}_k = \hat{a}_k^+ \hat{a}_k$ operating on $|N_1, N_2, \ldots, N_k \ldots>$ yields

$$\hat{N}_k |N_1, N_2, \ldots, N_k \ldots> = \hat{a}_k^+ \hat{a}_k |N_1, N_2, \ldots, N_k \ldots> = \sqrt{N_k}\, \hat{a}_k^+ |N_1, N_2, \ldots, N_k - 1, \ldots>$$

$$= N_k |N_1, N_2, \ldots, N_k, \ldots> \tag{10.6.20}$$

The number N_k is the eigenvalue of the operator $\hat{N}_k$ in the state $|\phi_N>$. Thus N_k is the number of particles in the kth state. The total number operator $\hat{N}$ operating on a state $|N_1, N_2, \ldots, N_k, \ldots>$ yields

$$\hat{N} |N_1, N_2, \ldots, N_k, \ldots> = \sum_k \hat{N}_k |N_1, N_2, \ldots, N_k \ldots> = \sum_k N_k |N_1, N_2, \ldots, N_k \ldots>$$

$$= N|N_1, N_2, \ldots, N_k \ldots > \tag{10.6.21}$$

where

$$N = \sum_k N_k$$

is the number of particles in the system. Thus the number N is the eigenvalue of the operator $\hat{N}$ in the state $|\phi_N>$. One particular member of basis is the vacuum state $|\phi_0>$ of the field. Thus

$$\hat{N}_k |\phi_0> = 0 \qquad \text{for all } k \tag{10.6.22}$$

and

$$<\phi_0 | \phi_0> = 1 \tag{10.6.23}$$

We can construct all the basis vectors by repeating the application of creation operation $\hat{a}_k^+$ on the vacuum state $|0>$. Thus

$$\hat{a}^+ |0> = |1> \equiv |\phi_1> \tag{10.6.24}$$

is the one-particle state and so on. Therefore, the eigenvalues of $\hat{N}_k$ are 0, 1, 2, ... This is applicable to the particles that obey Bose-Einstein statistics.

If the particles obey Fermi-Dirac statistics, the eigenvalue of the operator $\hat{N}_k$ should be limited to 0 and 1 (pauli's exclusion principle). In this case, the eigenvalue of $\hat{N}_k$ can be obtained by evaluating the square of the number operator. Thus

$$\hat{N}_k^2 = \hat{a}_k^+ \hat{a}_k \hat{a}_k^+ a_k = \hat{a}_k^+ (1 - \hat{a}_k^+ \hat{a}_k) \hat{a}_k = \hat{a}_k^+ \hat{a}_k - \hat{a}_k^+ \hat{a}_k^+ \hat{a}_k \hat{a}_k = \hat{a}_k^+ \hat{a}_k = \hat{N}_k \tag{10.6.25}$$

since from (10.6.11), $\hat{a}_k \hat{a}_k = \hat{a}_k^+ \hat{a}_k^+ = 0$. Thus

$$\hat{N}_k^2 - N_k = N_k (N_k - 1) = 0$$

giving $N_k = 0$ or 1. Hence, possible occupation number N_k for the state $\mathbf{k}$ can be 0 or 1 in agreement with Pauli's exclusion principle.

Substituting (10.6.6) in (10.6.5), we obtain the expression of the Hamiltonian operator of the field in terms of $\hat{a}_k$ and $\hat{a}_k^+$,

$$\hat{H} = (\hbar^2/2m) \sum_{k',k} <\mathbf{k}'|\nabla^2|\mathbf{k}> \hat{a}_{k'}^+ \hat{a}_k + \sum_{k'_1 k'_2 k_2 k_1} <\mathbf{k}'_1, \mathbf{k}'_2 |u| \mathbf{k}_2, \mathbf{k}_1> \hat{a}_{k'_1}^+ \hat{a}_{k'_2}^+ \hat{a}_{k_2} \hat{a}_{k_1}$$

where

$$<\mathbf{k}'|\nabla^2|\mathbf{k}> = \int d^3\mathbf{r}\, u_{k'}^*(\mathbf{r}) \nabla^2 u_k(\mathbf{r}) \tag{10.6.27}$$

and

$$<\mathbf{k}'_1, \mathbf{k}'_2 |u| \mathbf{k}_2, \mathbf{k}_1> = \int\int d^3\mathbf{r}_1\, d^3\mathbf{r}_2\, u_{k'}(\mathbf{r}_1)\, u_{k'}(\mathbf{r}_2)\, u(\mathbf{r}_1, \mathbf{r}_2)\, u_{k_2}(\mathbf{r}_2)\, u_{k_1}(\mathbf{r}_1) \tag{10.6.28}$$

Let the single-particle wave functions be

$$u_k(r) = (1/V^{1/2}) \exp(i\mathbf{k}.\mathbf{r}) = (1/V^{1/2}) \exp(i\mathbf{P}.\mathbf{r}/\hbar) \tag{10.6.29}$$

where $\mathbf{P} = \hbar\mathbf{k}$ is the momentum of the (spinless) particle; then,

$$\langle \mathbf{k}'|\nabla^2|\mathbf{k}\rangle = (1/V)\int d^3\mathbf{r}\, \exp(-i\mathbf{P}'.\mathbf{r}/\hbar)(-P^2/\hbar^2)\exp(i\mathbf{P}.\mathbf{r}/\hbar) = -(P^2/\hbar^2)\,\delta_{k'k} \tag{10.6.30}$$

and

$$\langle \mathbf{k}_1', \mathbf{k}_2'|u|\mathbf{k}_2,\mathbf{k}_1\rangle = (1/V^2)\int\int d^3\mathbf{r}_1\, d^3\mathbf{r}_2 \exp(i(\mathbf{P}_1-\mathbf{P}_1').\mathbf{r}_1/\hbar)\, u(\mathbf{r}_1,\mathbf{r}_2)\exp(i(\mathbf{P}_2-\mathbf{P}_2').\mathbf{r}_2/\hbar) \tag{10.6.31}$$

Since the total momentum is conserved in the collision, i.e

$$\mathbf{P}_1+\mathbf{P}_2 = \mathbf{P}_1'+\mathbf{P}_2'$$

the matrix element (10.6.31), can be expresed as

$$\langle \mathbf{k}_1', \mathbf{k}_2'|u|\mathbf{k}_2,\mathbf{k}_1\rangle \equiv u_{P_1P_2}^{P_1'P_2'} = (1/V^2)\int\int d^3\mathbf{r}_1\, d^3\mathbf{r}_2 \exp(-i(\mathbf{P}_2'-\mathbf{P}_2).(\mathbf{r}_2-\mathbf{r}_1)/\hbar)\, u(\mathbf{r}_1,\mathbf{r}_2)$$

$$= (1/V)\int d^3\mathbf{r}\exp(i\mathbf{P}.\mathbf{r}/\hbar)\, u(\mathbf{r}) \tag{10.6.32}$$

where P is the momentum transfer in the collision, i.e.

$$\mathbf{P} = (\mathbf{P}_2'-\mathbf{P}_2) = -(\mathbf{P}_1'+\mathbf{P}_1)$$

Substituting (10.6.30) and (10.6.32) in (10.6.26), we obtain an expression for the Hamiltonian operator of the field.

$$\hat{H} = \sum_P (P^2/2m)\,\hat{a}_P^+\hat{a}_P + (1/2)\sum u_{P_1P_2}^{P_1'P_2'}\,\hat{a}_{P_1'}^+\hat{a}_{P_2'}^+\,\hat{a}_{P_2}\hat{a}_{P_1} \tag{10.6.33}$$

The summation in the second term of (10.6.33) goes over only those values of the momenta $\mathbf{P}_1$, $\mathbf{P}_2$ and $\mathbf{P}_1'$, $\mathbf{P}_2'$ which conserve the total momentum of the particles. The first term of (10.6.33) is the kinetic energy operator of the field, while the second term is the potential energy operator.

Equation (10.6.33) represents the Hamiltonian operator of the spinless particles. In the case of spin-half fermions, the single-particle states are the characterised not only by the momentum **P** but also by the σ. Accordingly, the Hamiltonian operator for spin-half fermions takes the form

$$\hat{H} = \sum_{P,\sigma}(P^2/2m)\,\hat{a}_{P\sigma}^+\hat{a}_{P\sigma} + (1/2)\sum u_{P_1\sigma_1,P_2\sigma_2}^{P_1'\sigma_1',P_2'\sigma_2'}\,\hat{a}_{P_1'\sigma_1'}^+\hat{a}_{P_2'\sigma_2'}^+\hat{a}_{P_2\sigma_2}\hat{a}_{P_1\sigma_1} \tag{10.6.34}$$

The summation in the second term of (10.6.34) again goes over only those states which confirm the conservation of both momentum and spin.

From (10.6.6) it is easy to see that the operator $\hat{\psi}^+(\mathbf{r})$ creates a particle at the point r in the field while $\hat{\psi}(\mathbf{r})$ annihilates the particle at the point **r**. However, the process of creation or annihilation is associated with the point **r** of the field. We can easily verify that for both bosons and fermions, the operators $\hat{N}$ and $\hat{H}$ commute i.e.

$$[\hat{N},\hat{H}] = 0 \tag{10.6.35}$$

Thus, the operator $\hat{N}$ and $\hat{H}$ can be simultaneously diagonalised.

The basis vector (10.6.15) for bosons is obtained from

$$|\phi_0\rangle = [N_1!\, N_2! \ldots N_k! \ldots]^{-1/2} (\hat{a}_1^+)^{N1} (\hat{a}_2^+)^{N2} \ldots (\hat{a}_k^+)^{Nk} \ldots |\phi_0\rangle \tag{10.6.36}$$

The basic vector (10.6.36) is a simultaneous eigenket of all N's belonging to the eigenvalues $N_1, N_2, \ldots$. The various kets (10.6.36) form a complete set for the dynamical system consisting of N bosons. However, in case of fermions, where the eigenvalues N_k's are either zero or unity, the basic vector is written as

$$|\phi_N\rangle = [N_a, N_b, \ldots\rangle = \hat{a}_a^+ \hat{a}_b^+ \ldots \hat{a}_g^+ |\phi_0\rangle \tag{10.6.37}$$

which is normalised and is a simultaneous eigenfunction of all N's belonging to the eigenvalues unity for $N_a, N_b, \ldots N_g$ and zero for others.

In the following sections, we apply this formalism which is commonly known as second quantisation to study the low temperature behaviour of imperfect gases.

10.7. Imperfect Bose Gas

We consider an imperfect gas of N identical (spinless) bosons, each of mass m contained in a volume V at low temperature T. By an imperfect gas we mean a dilute system of weakly interacting particles, so that the interparticle interactions are treated as a perturbation and the system differs slightly from the ideal gas.

The interparticle potential must have a finite range, and is such that the two-body bound state does not exist. For such a system, the potential is strongly repulsive at small distance. It is well known that the low temperature behaviour of a two-particle system depends only on an equivalent hard sphere diameter a, known as the scattering length. For such a system the basic parameters of the problem are

$\lambda = (2\pi\hbar^2/mkT)^{1/2}$ (thermal wavelength)

$l = v^{1/3} = (V/N)^{1/3}$ (mean interparticle distance)

a = scattering length.

We consider the Bose gas at such densities and temperatures, where

$a/l \ll 1$ (low density)

$a/\lambda \ll 1$ (low temperature)

We now develop a perturbation method to calculate the leading terms in the expansion of the thermodynamic properties of the system in powers of quantities a/λ and a/l.

We assume binary interaction between particles and apply the method of second quantisation to the energy spectrum of low excited states of an imperfect Bose gas. The Hamiltonian of the quantised field of the (spinless) bosons is given by

$$\hat{H} = \hat{T} + \hat{V} \tag{10.7.1}$$

where $\hat{T}$ and $\hat{V}$ are respectively the kinetic energy and potential energy operators:

$$\hat{T} = \sum_{P} \in (P)\, \hat{a}_P^{+} \hat{a}_P \tag{10.7.2}$$

$$\hat{V} = (1/2) \sum u_{P_1 P_2}^{P_1' P_2'} \hat{a}_{P_1'}^{+} \hat{a}_{P_2'}^{+} \hat{a}_{P_2} \hat{a}_{P_1} \tag{10.7.3}$$

Here $\in (P) = P^2/2m$ is the eigenvalue of the kinetic energy operator $-(\hbar/2m)\nabla^2$; and $\hat{a}_P^{+}$ and $\hat{a}_P$ are the creation and annihilation operators for a free particle with momentum **P**, which is represented by the wave function

$$\psi_P(r) = (1/V^{1/2}) \exp(\mathbf{P}.\mathbf{r}/\hbar) \tag{10.7.4}$$

The summation of (10.7.3) is over all values of the momenta of a pair of particles, with the condition that the total momentum is conserved in the collision, i.e.

$$\mathbf{P}_1 + \mathbf{P}_2 = \mathbf{P}_1' + \mathbf{P}_2'$$

The matrix elements $u_{P_1 P_2}^{P_1' P_2'}$ is expressed as

$$u_{P_1 P_2}^{P_1' P_2'} = (1/V^2) \int d\mathbf{r}_1 d\mathbf{r}_2 \exp(i(\mathbf{P}_1 - \mathbf{P}_1').\mathbf{r}_1/\hbar)\, u(|\mathbf{r}_2 - \mathbf{r}_1|) \exp(i(\mathbf{P}_2 - \mathbf{P}_2').\mathbf{r}_2/\hbar)$$

$$= (1/V) \int d\mathbf{r} \exp(-i\mathbf{P}.\mathbf{r}/\hbar)\, u(\mathbf{r}) \tag{10.7.5}$$

where **P** is the particle momentum transfer in the collision, where

$$\mathbf{P} = (\mathbf{P}_2' - \mathbf{P}_2) = -(\mathbf{P}_1' - \mathbf{P}_1)$$

The effective scattering cross-section for binary collision is characterised by the scattering length a given by

$$a = (m/4\pi\hbar^2) \int u(r) \exp(i\mathbf{P}.\mathbf{r}/\hbar)\, d\mathbf{r} \tag{10.7.6}$$

where m is the mass of a colliding particle and **P** is the momentum transfer in the collision. For low energy scattering (i.e. in slow collision), $\mathbf{P}.\mathbf{r} \ll 1$ throughout the important range of integration, and (10.7.6) becomes

$$a = m u_0 / 4\pi\hbar^2 \tag{10.7.7}$$

with

$$u_0 = \int u(r)\, d\mathbf{r} \tag{10.7.8}$$

Thus we have

$$u_0 = 4\pi\hbar^2 a/m \tag{10.7.9}$$

At low temperature, where $a/\lambda \ll 1$, the particle momenta are small and hence the matrix elements in the sum of (10.7.3) can be replaced by their values at $\mathbf{P} = 0$. Substituting this value in (10.7.3), we have

$$\hat{V} = (u_0/2V) \Sigma \hat{a}^{+}_{P_1} \hat{a}^{+}_{P_2} \hat{a}_{P_2} \hat{a}_{P_1} \tag{10.7.10}$$

and hence,

$$\hat{H} = \sum_{P} \epsilon(P) \hat{a}^{+}_{P} \hat{a}_{P} + (u_0/2V) \Sigma \hat{a}^{+}_{P_1} \hat{a}^{+}_{P_2} \hat{a}_{P_2} \hat{a}_{P_1} \tag{10.7.11}$$

We apply the perturbation theory to the Hamiltonian (10.3.11). The perturbation theory is based on the concept that at low temperatures, most of the particles of the system are in the ground state and the number of particles in the excited states are very small. Let N be the total number of particles in the system, then

$$\hat{N} = \sum_{P} \hat{a}^{+}_{P} \hat{a}_{P} \tag{10.7.12}$$

In the ground state of an ideal Bose gas, all the particles are in the condensate state with zero energy (i.e. $\mathbf{P} = 0$). Thus $N_0 = N$ and $N_P = 0$ for $\mathbf{P} = 0$. The interaction potential acts as a small correction in a weakly interacting gas, so its ground state energy is slightly higher than that of the ideal gas. Hence, the number of particles N_0 in the condensate will be much larger than those above the condensate, i.e. $N_0 \gg N - N_0$. In the low excited state, the occupation number N_P are also small compared to N_0. Hence

$$\hat{a}^{+}_{0} \hat{a}_{0} = N_0 = N - \sum_{P \neq 0} \hat{a}^{+}_{P} \hat{a}_{P} \tag{10.7.13}$$

From the boson commutation relation

$$\hat{a}_0 \hat{a}^{+}_{0} - \hat{a}^{+}_{0} \hat{a}_0 = 1$$

we find that

$$\hat{a}_0 \hat{a}^{+}_{0} = \hat{a}^{+}_{0} \hat{a} + 1 \quad \hat{a}^{+}_{0} \hat{a}_0$$

since $\hat{N}_0 = \hat{a}^{+}_{0} \hat{a}_0 \gg 1$. Thus, we may ignore the commutation relation for the operators $\hat{a}_0$, $\hat{a}^{+}_{0}$, and treat them as ordinary numbers, i.e.

$$\hat{a}_0 = \hat{a}^{+}_{0} = \hat{N}_0^{1/2}$$

In order to apply the perturbation theory, we expand the quadruple sum in (10.7.11) in terms of the small quantities $\hat{a}_P \hat{a}^{+}_{P}$ ($P \neq 0$). Thus,

$$\Sigma \hat{a}^{+}_{P_1} \hat{a}^{+}_{P_2} \hat{a}_{P_2} \hat{a}_{P_1} = \hat{a}^{+}_{0} \hat{a}^{+}_{0} \hat{a}_0 \hat{a}_0 + \sum_{P \neq 0} (\hat{a}^{+}_{P} \hat{a}^{+}_{P} \hat{a}_0 \hat{a}_0 + \hat{a}^{+}_{P} \hat{a}^{+}_{0} \hat{a}_P \hat{a}_0 + \hat{a}^{+}_{P} \hat{a}^{+}_{0} \hat{a}_0 \hat{a}_P + \hat{a}^{+}_{0} \hat{a}^{+}_{P} \hat{a}_P \hat{a}_0 + \hat{a}^{+}_{0} \hat{a}^{+}_{P} \hat{a}_0 \hat{a}_P$$

$$+ \hat{a}_0^+ \hat{a}_0^+ \hat{a}_P \hat{a}_P) + \ldots \tag{10.7.14}$$

The zeroth order term of the expansion is

$$\hat{a}_0^+ \hat{a}_0^+ \hat{a}_0 \hat{a}_0 = \hat{a}_0^+ (\hat{a}_0 \hat{a}_0^+ - 1)\hat{a}_0 = \hat{a}_0^+ \hat{a}_0 \hat{a}_0^+ \hat{a}_0 - \hat{a}_0^+ \hat{a}_0 = N_0^2 - N_0 \quad N_0^2 \tag{10.7.15}$$

and $\hat{a}_0^+$ and $\hat{a}_0$ appearing in the second term of the expansion are treated as an ordinary number $N_0^{1/2}$. Then (10.7.14) can be written as

$$\Sigma \hat{a}_{P_1}^+ \hat{a}_{P_2}^+ \hat{a}_{P_2} \hat{a}_{P_1} = N_0^2 + N_0 \sum_{P \neq 0} (\hat{a}_P^+ \hat{a}_{-P}^+ + \hat{a}_P \hat{a}_{-P} + 4 \hat{a}_P^+ \hat{a}_P)$$

$$= N^2 + N \sum_{P \neq 0} (\hat{a}_P^+ \hat{a}_{-P}^+ + \hat{a}_P \hat{a}_{-P} + 2 \hat{a}_P^+ \hat{a}_P) \tag{10.7.16}$$

Substituting this value in (10.7.11), we obtain an expression for the Hamiltonian correct to the second order correction

$$\hat{H} = (N^2 u_0/2V) + \{ \sum_{P \neq 0} (\epsilon(P) + (Nu_0/V)) \hat{a}_P^+ \hat{a}_P + (Nu_0/2V) \sum_{P \neq 0} (\hat{a}_P^+ \hat{a}_{-P}^+ + \hat{a}_P \hat{a}_{-P}) \} \tag{10.7.17}$$

This equation is given in terms of the quantity u_0, which in turn can be expressed in terms of the scattering length a. Equation (10.7.5) provides an approximate result for u_0, which can be used to evaluate the second terms of (10.7.17). However, a better approximation for u_0 is required to evaluate the first term. For this we apply the theory of transition probability of a system under the influence of a constant perturbation. If the probability of a given transition of a system is determined by the matrix element V_{00} in the first approximation, then the transition probability in the second approximation is given by

$$V_{00} + \sum_n (V_{0n} V_{n0}/(E_0 - E_n))$$

where the summation is over all states of the unperturbed system. In the present case, we are dealing with a collision in two-particle system (with reduced mass m/2), V_{00} becomes u_{00}^{00}, where

$$u_{00}^{00} = (1/V) \int u(r)\, dr = u_0/V \tag{10.7.18}$$

For other matrix elements, we use (10.7.5). Then, in the second approximation, we must replace u_0 of the first term of (10.7.17) by

$$u_0 + (1/V) \sum_{P \neq 0} |dr \exp(iP.r/\hbar) u(r)|^2/(-P^2/m) \qquad u_0 - (u_0^2/V) \sum_{P \neq 0} (m/P^2)$$

$$u_0 (1 - (u_0/V) \sum_{P \neq 0} (m/P^2)) \tag{10.7.19}$$

Then, instead of (10.7.7), we have

$$a = (m/4\pi\hbar^2)u_0 (1 - (u_0/V) \sum_{P\neq 0} (m/P^2)) \tag{10.7.20}$$

which gives

$$u_0 \quad (4\pi\hbar^2/m)\, a\, (1 + (4\pi\hbar^2 a/mV) \sum_{P\neq 0} (m/P^2)) \tag{10.7.21}$$

Substituting (10.7.21) in (10.7.17), we get

$$\hat{H} = (UN^2/2V)\,(1 + (U/V) \sum_{P\neq 0} (m/P^2)) + (1/2) \sum_{P\neq 0} (\in (P) + (UN/V))\, (\hat{a}_P^+ \hat{a}_P + \hat{a}_{-P}^+ \hat{a}_{-P})$$

$$+ (UN/2V) \sum_{P\neq 0} (\hat{a}_P^+ \hat{a}_{-P}^+ + \hat{a}_P \hat{a}_{-P}) \} \tag{10.7.22}$$

where

$$U = (4\pi\hbar^2 a/m) \tag{10.7.22}$$

and

$$\hat{N}(\mathbf{P}) = \hat{a}_P^+ \hat{a}_P \equiv (1/2)\, (\hat{a}_P^+ \hat{a}_P + \hat{a}_{-P}^+ \hat{a}_{-P}) \tag{10.7.24}$$

Here $\hat{N}(\mathbf{P})$ is the occupation number with $P \neq 0$.

The energy level of the system is determined from the diagonal element of the Hamiltonian. But the last term of (10.7.22) is nondiagonal. In order to diagonalise it, Bogolubov (1947) has introduced a linear transformation of the operators $\hat{a}_P$ and $\hat{a}_{-P}^+$

$$\hat{b}_P = (\hat{a}_P - \alpha_P \hat{a}_{-P})/(1 - \alpha_P^2)^{1/2}$$

$$\hat{b}_P^+ = (\hat{a}_P^+ - \alpha_P \hat{a}_{-P}^+)/(1 - \alpha^2)^{1/2} \tag{10.7.25}$$

where α_P is the ordinary number, which is the positive eigenvalue of momentum $\mathbf{P}$ and less than unity, i.e.

$$\alpha_P = \alpha_{-P}$$

We can show the relations inverse to (10.7.25)

$$\hat{a}_P = (\hat{b}_P + \alpha_P \hat{b}_{-P}^+)/(1 - \alpha_P^2)^{1/2}$$

$$\hat{a}_P^+ = (\hat{b}_P^+ + \alpha_P \hat{b}_{-P})/(1 - \alpha_P^2)^{1/2} \tag{10.7.26}$$

The new operators $\hat{b}_P$ and $\hat{b}_P^+$ satisfy the same commutation relations as the old operators $\hat{a}_P$ and $\hat{a}_P^+$ namely

$$[\hat{b}_P, \hat{b}_{P'}^+] = \delta_{PP'} \tag{10.7.27a}$$

$$[\hat{b}_P, \hat{b}_P] = [\hat{b}_P^+, \hat{b}_{P'}^+]_{\mp} = 0 \tag{10.7.27b}$$

With the aid of Eqs. (10.7.26) and (10.7.27), it is easy to show that

$$\hat{a}_P^+ \hat{a}_P + \hat{a}_{-P}^+ \hat{a}_{-P} = (1 - \alpha_P^2)^{-1} [(1 + \alpha_P^2)(\hat{b}_P^+ \hat{b}_P + \hat{b}_{-P}^+ \hat{b}_{-P}) + 2\alpha_P(\hat{b}_P^+ \hat{b}_{-P}^+ + \hat{b}_P \hat{b}_{-P}) + 2\alpha_P^2] \quad (10.7.28a)$$

and

$$\hat{a}_P^+ \hat{a}_{-P}^+ + \hat{a}_P \hat{a}_{-P} = (1 - \alpha_P^2)^{-1} [(1 + \alpha_P^2)(\hat{b}_P^+ \hat{b}_{-P}^+ + \hat{b}_P \hat{b}_{-P}) + 2\alpha_P(\hat{b}_P^+ \hat{b}_P + \hat{b}_{-P}^+ \hat{b}_{-P}) + 2\alpha_P^2] \quad (10.7.28b)$$

Substituting these values in (10.7.22), we get

$$\hat{H} = (UN^2/2V)(1 + (U/V)\sum_{P\neq 0}(m/P^2)) + \sum_{P\neq 0}(1 - \alpha_P^2)^{-1}[(\epsilon(P) + (UN/V))\alpha_P^2 + (UN/V)\alpha_P]$$

$$+ (1/2)\sum_{P\neq 0}(1 - \alpha_P^2)^{-1}[(\epsilon(P) + (UN/V))(1 + \alpha_P^2) + (2UN/V)\alpha_P](\hat{b}_P^+ \hat{b}_P + \hat{b}_{-P}^+ \hat{b}_{-P})$$

$$+ (1/2)\sum_{P\neq 0}(1 - \alpha_P^2)^{-1}[2(\epsilon(P) + (UN/V))\alpha_P + (UN/V)(1 + \alpha_P^2)](\hat{b}_P^+ \hat{b}_{-P}^+ + \hat{b}_P \hat{b}_{-P}) \quad (10.7.29)$$

The last terms of (10.7.29) is nondiagonal and vanishes if

$$2(\epsilon(P) + (UN/V))\alpha_P + (UN/V)(1 + \alpha_P^2) = 0 \quad (10.7.30)$$

which gives

$$\alpha_P = (V/UN)[-(\epsilon(P) + (UN/V)) + \sqrt{\{(\epsilon(P) + (UN/V))^2 - (UN/V)^2\}}]$$

$$= (V/UN)[E(P) - \epsilon(P) - (UN/V)] \quad (10.7.31)$$

where

$$E(P) = \sqrt{\{(\epsilon(P) + (UN/V))^2 - (UN/V)^2\}} = \sqrt{\{(\epsilon(P))^2 + (2UN/V)^2 \epsilon(P)\}} \quad (10.7.32)$$

In deriving (10.7.21), only the positive sign before the radical is taken so that the excited states have positive energy. Equation (10.7.30) can be rearranged to give

$$(1 - \alpha_P^2)^{-1}[(\epsilon(P) + (UN/V))\alpha_P^2 + (UN/V)] = (UN/2V)\alpha_P \quad (10.7.33a)$$

and

$$(1 - \alpha_P^2)^{-1}[(\epsilon(P) + (UN/V))(1 + \alpha_P^2) + (2UN/V)\alpha_P] = (UN/V)\alpha_P + (\epsilon(P) + (UN/V)) \quad (10.7.33b)$$

Substituting Eqs.(10.7.33) and (10.7.3) in Eq.(10.7.29) we obtain the Hamiltonian in the digonalised form:

$$\hat{H} = E_0 + (1/2)\sum_{P\neq 0} E(P)(\hat{b}_P^+ \hat{b}_P + \hat{b}_{-P}^+ \hat{b}_{-P}) = E_0 + \sum_{P\neq 0} E(P)\hat{b}_P^+ \hat{b}_P \quad (10.7.34)$$

where

$$E_0 = (UN^2/2V) + (1/2)\sum_{P\neq 0}[E(P) - \epsilon(P) - (UN/V) + (UN/V)^2 (m/P^2)]$$

$$= (UN^2/2V) + (1/2) \sum_{P\neq 0} [E(P) - (P^2/2m) - (UN/V) + (UN/V)^2 (m/P^2)] \qquad (10.7.35)$$

The behaviour of the operators $\hat{b}_P^+$ and $\hat{b}_P$ shows that $\hat{b}_P^+$ and $\hat{b}_P$ are the creation and annihilation operators for quasi-particles (elementary excitations of the system), obeying Bose-Einstein statistics. The energy E(P) of quasi particle is given by (10.7.32). The quantity $\hat{b}_P^+ \hat{b}_P = \hat{n}(P)$ is the particle number operator for the quasi-particles with momentum **P**, which differs from the occupation number $\hat{N}(P)$ for the actual particles of this gas.

In Eq.(10.7.34), E_0 is the ground state energy of the dilute Bose gas and is given by (10.7.35), and $\sum_{P\neq 0} E(P)\, \hat{b}_P^+ \hat{b}_P = \sum_{P\neq 0} E(P)\, \hat{n}(P)$ is the excitation energy of the system. Thus a quasi-particle model of energy E(**P**) describes successfully the weakly excited state of the dilute Bose gas.

Substituting (10.7.23) in (10.7.35) and replacing the summation over **P** by integration.

$$\sum_{P\neq 0} \rightarrow (V/h^3) \int dP = (4\pi V/(2\pi\hbar)^3) \int_0^\infty dP\, P^2,$$

we get

$$E_0 = (2\pi a\hbar^2 N^2/mV) + (2\pi V/(2\pi\hbar)^3) \int_0^\infty dP\, P^2 [\{(P^2/2m)^2 + (4\pi a\hbar^2 N/mV)(P^2/m)\}^{1/2} - (P^2/2m)^2$$

$$- (4\pi a\hbar^2 N/mV) + (4\pi a\hbar^2 N/mV)^2 (m/P^2)\,] \qquad (10.7.36)$$

Introducing a dimensionless parameter x, defined by

$$x = (V/8\pi a\hbar^2 N)^{1/2} P$$

we can write the ground state energy E_0 in the form

$$E_0 = (2\pi a\hbar^2 N^2/mV) [1 + (128Na^3/\pi V)^{1/2} \int_0^\infty dx\, x^2 \{x(x^2+2)^{1/2} - 1 - x^2 + (1/2x^2)\}] \qquad (10.7.37)$$

The integral of (10.7.37) is evaluated to be $(128)^{1/2}/15$. Hence the result for the ground state energy is

$$E_0/N = (2\pi a\hbar^2/m)\rho [1 + (128/15\pi^{1/2})(\rho a^3)^{1/2}\,] \qquad (10.7.38)$$

where $\rho = N/V$ is the particle density of the system. This result was first derived by Lee and Yang by keeping the first two terms of the expansion of E_0/N in the powers of $(\rho a^3)^{1/2}$. The first term of (10.7.38) is the zeroth order result, and the second term is the correlation over it, which arises due to the deviation of the dilute Bose gas from the ideal state.

The ground state pressure of the system is given by

$$P_0 = -(\partial E_0/\partial V)_N = \rho^2(\partial(E_0/N)/\partial\rho) = (2\pi a\hbar^2/m)\rho^2 [1 + (64/5\pi^{1/2})(\rho a^3)^{1/2}\,] \qquad (10.7.39)$$

The velocity of sound wave C_0 in the gas is

$$C_0 = \sqrt{(VK_T/mN)} = \sqrt{\{(V^2/mN)(\partial^2 E_0/\partial V^2)\}}$$

$$C_0^2 = (1/m)(\partial/\partial\rho)[\rho^2(\partial(E_0/N)/\partial\rho)]$$

$$= (4\pi a\hbar^2/m^2)\rho[1 + (16/\pi^{1/2})(\rho a^3)^{1/2}] \quad (10.7.40)$$

where K_T is the isothermal compressibility of the gas.

The momentum distribution of the real particles of the gas can be determined by calculating the ground state expectation values of the number operators $\hat{a}_P^+ \hat{a}_P$. Thus,

$$< N(P) > = <\hat{a}_P^+ \hat{a}_P> = <\psi_0 |\hat{a}_P^+ \hat{a}_P| \psi_0> \quad (10.7.41)$$

Substituting (10.7.26) and using the fact that $\hat{b}_P|\psi_0> = 0$, we get

$$<N(P) > = (\alpha_P^2/(1-\alpha_P^2)) <\psi_0 |\hat{b}_{-P} \hat{b}_{-P}^+| \psi_0> = (\alpha_P^2/(1-\alpha_P^2)) \quad (10.7.42)$$

Here we have made use of the fact that

$$\hat{b}_{-P} \hat{b}_{-P}^+ - \hat{b}_{-P}^+ \hat{b}_{-P} = 1$$

and in the ground state $\hat{b}_{-P}^+ \hat{b}_{-P} = 0$ for all $\mathbf{P} \neq 0$. Substituting the value of α_P from (10.7.31), we obtain ($\mathbf{P} \neq 0$)

$$<N(P)> = ((1 + x^2)/2x(x^2 + 2)^{1/2}) - (1/2) \quad (10.7.43)$$

where $x = P(8\pi a\hbar^2\rho)^{-1/2}$. Then the total number of excited particles in the ground state of the system is given by

$$\sum_{P\neq 0} <N(P)> = \sum_{P\neq 0} (\alpha_P^2/(1-\alpha_P^2)) = (4\pi V/(2\pi\hbar)^3) \int_0^\infty dP\, P^2 [\alpha_P^2/(1-\alpha_P^2)]$$

$$N[(32/\pi)(\rho a^3)]^{1/2} \int_0^\infty dx [x\{((1+x^2)/(x^2+2)^{1/2}) - x\}] \quad (10.7.44)$$

The integral is evaluated to be $2^{1/2}/3$. Thus the result for the average number of total particles with $P \neq 0$ is given by

$$\sum_{P\neq 0} <N(P)> = N(8/3\pi^{1/2})(\rho a^3)^{1/2} \quad (10.7.45)$$

and hence the average number of total particles with $P = 0$ is

$$<N_0> = N - \sum_{P\neq 0} <N(P)> = N[1 - (8/3\pi^{1/2})(\rho a^3)^{1/2}] \quad (10.7.46)$$

Thus, we conclude that a small fraction of particles of a dilute Bose gas are excited even at absolute zero. This is due to the deviation of the Bose gas from the ideal state.

Let us now consider energy spectrum (10.7.32) of the elementary excitations (quasi-particles) in a dilute Bose gas. It can be rewritten as

$$E(P) = [(\epsilon(P) + mC^2)^2 - (mC^2)^2]^{1/2} = [(\epsilon(P))^2 + 2mC^2\epsilon(P)]^{1/2} \quad (10.7.47)$$

where

$$C = (4\pi a\hbar^2\rho)^{1/2}/m \quad (4\pi a\hbar^2\rho_0)^{1/2}/m \quad (10.7.48)$$

In the high and low temperature limits, (10.7.47) is expressed in the forms

$$E(P) = \epsilon(P) + mC^2$$

$$= (P^2/2m) + mC^2 \qquad \text{when } P \to \infty \quad (10.7.49)$$

$$E(P) = 2mC^2\epsilon(P)$$

$$= CP \qquad \text{when } P \to 0 \quad (10.7.50)$$

Thus at small momenta, the excitation energy in a dilute Bose is linearly dependent on its momenta and corresponds to the phonon part of the energy spectrum of a Bose gas. For large values of P, the energy approaches the classical limit E(P) $P^2/2m$. The energy dispersion curve is shown in Fig.10.2. Solid lines represent the low and high energy regions of the curve. The dotted line of the curve represents the intermediate region. This theory is not predicting its precise form. This is not surprising, because the theory is intended for a dilute Bose gas and not for liquid He II.

10.8. Bose-Einstein Phase-Transition in an Imperfect Bose System

In this section, we consider a system of N identical interacting bosons, each of mass m, enclosed in a volume V at a temperature T. The bosons interact with one another through binary collisions. The Hamiltonian for such a system is given by (10.7.34), i.e.

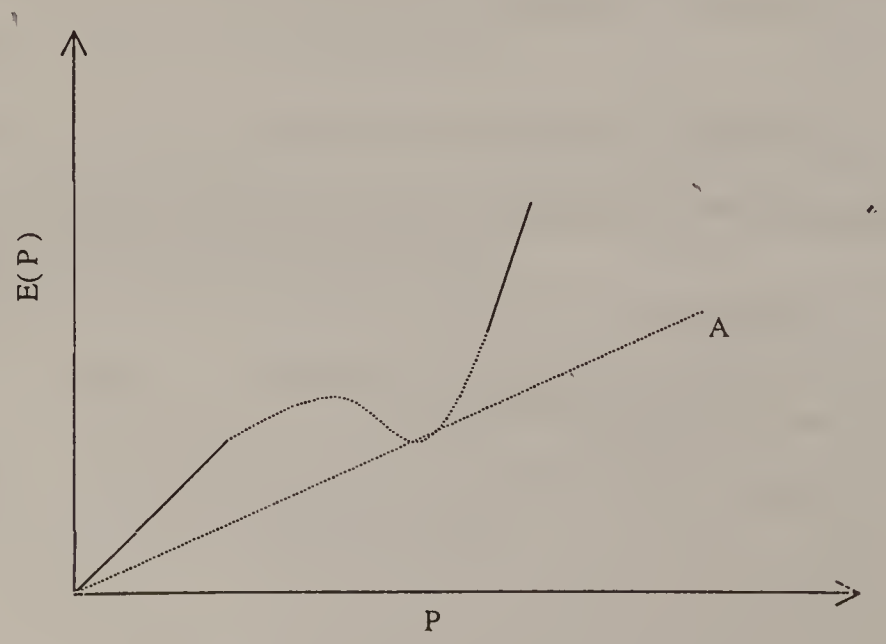


Fig.10.2. Energy-dispersion curve

$$H = E_0 + \sum_{P \neq 0} E(P)n(P) \tag{10.8.1}$$

where n(P) is the number of quasi-particles with momentum $P \neq 0$. The excitation energy E(P) per particle is given by (10.7.32). In the transition region, where P is large, the excitation energy is given by

$$E(P) = (P^2/2m) + mc^2 = (P^2/2m) + (4\pi a\hbar^2/m)\,\rho_0 \tag{10.8.2}$$

where a is the scattering length, defined by (10.7.6), from which we obtain

$$4\pi a\hbar^2/m = \int \mathbf{dr}\, u(r)\,[1 + i(\mathbf{P}.\mathbf{r}/\hbar) + (1/2)\,(\mathbf{P}.\mathbf{r}/\hbar)^2 + \ldots\,]$$

For a spherically symmetric potential, the linear term vanishes. Then, we get

$$4\pi a\hbar^2/m = u(P) = u_0 + b_0P^2$$

where

$$u_0 = \int \mathbf{dr}\, u(r)$$

$$b_0 = -(1/6\hbar^2) \int \mathbf{dr}\, r^2u(r)$$

Thus the inter particle potential is assumed to be a quadratic function of momentum. Then the excitation energy becomes

$$E(P) = (P^2/2m)\,\rho_0u_0 + \rho_0b_0P^2 \tag{10.8.3}$$

In the region of transition, the system may be considered as a mixture of two phases: one phase containing particles with $P = 0$ and the other with $P \neq 0$. In the state $P \neq 0$, the total energy is the kinetic energy plus the interaction energy. Thus the excitation energy per particle for state $P \neq 0$ is written as

$$E(P) = (P^2/2m^*) + \rho_0u_0 \tag{10.8.4}$$

where

$$(1/m^*) = (1/m) + 2\rho_0b_0$$

m^* is known as the effective mass. Thus in the effective mass approximation, the energy has the same momentum dependence as a free particle of mass m^*. The mean occupation number of this state is

$$\langle n(E)\rangle = 1/(e^{\beta E(P)} - 1) \tag{10.8.5}$$

where $\beta = 1/kT$.

We consider the imperfect Bose gas of spinless particles. The total number of particles in the state $P \neq 0$ is expressed by

$$N_e = N - N_0 = (4\pi V/h^3) \int_0^\infty P^2 dP/(e^{\beta E(P)} - 1)$$

$$= (4\pi V/h^3) \int_0^\infty P^2 dP/(z^{-1} \exp(P^2/2m^*KT) - 1) \qquad (10.8.6)$$

where

$$z = \exp(-\rho_0 u_0/kT) \qquad (10.8.7)$$

(10.8.6) can be evaluated to give [see eq.(7.2.5)]

$$N_e \equiv N - N_0 = V(4\pi m^* kT/h^2)^{3/2} g_{3/2}(z) \qquad (10.8.8)$$

Hence the number density of the particles in the states $P \neq 0$ is

$$\rho_e = \rho - \rho_0 = \lambda^{-3} g_{3/2}(z) \qquad (10.8.9a)$$

and

$$\rho = \rho_0 + \lambda^{-3} g_{3/2}(z) \qquad (10.8.9b)$$

where ρ_0 is the number density of particles in the state $P = 0$.

Let T_0 be the transition temperature at which $\rho_0 = 0$ and $z = 1$. In this case N_e is practically identical to the total number of particles N. Thus,

$$\rho = N/V = (2\pi m^* kT_0/h^2)^{3/2} \xi(3/2) \qquad (10.8.10)$$

Hence T_0 for an imperfect gas is expressed as

$$T_0 = (\rho/\xi(3/2))^{2/3} (h^2/2\pi m^* k) \qquad (10.8.11)$$

which is a function of density ρ and effective mass m^*. When bosons are assumed to be noninteracting, the transition temperature T_c is given by [see Eq.(7.2.12)]

$$T_c = (\rho/\xi(3/2))^{2/3} (h^2/2\pi mk) \qquad (10.8.12)$$

From (10.8.11) and (10.8.12), we arrive at the conclusion that

$$T_0 m^* = T_c m$$

or

$$T_0 = (m/m^*) T_c \qquad (10.8.13)$$

Thus the interparticle potential shifts the transition temperature by an amount

$$\Delta T_0/T_c = (T_0 - T_c)/T_c = (m/m^*) - 1 = 2mb_0\rho_0 \quad 2mb_0\rho \tag{10.8.14}$$

When $m/m^* < 1$, then $T_0 < T_c$, and the particles of such a system will interact via repulsive potential. Thus a purely repulsive potential lowers the transition temperature. Liquid He^4 is such a system for which $T_c = 3.13$ K and $T_o = 2.186$ K. On the other hand, if $m/m^*>1$, then $T_o>T_c$ and the particles of such a system will interact via attractive potential.

Luban and Grobmon (1966) have used the repulsive pair potential of the form

$$u(P) = u_0(1 - (P^2/P_0^2)) \tag{10.8.15}$$

where $u_0 > 0$, to study the properties of an imperfect Bose system. For this potential, the effective mass m^* is given by

$$m^* = m(1 - (2m\rho_0 u_0/P_0^2))^{-1} > m \tag{10.8.16}$$

They have found that $m^*/m = 5.52$

10.9. Imperfect Fermi Gas

We consider an imperfect gas of N identical (spin(1/2)) fermions, each of mass m, enclosed in a volume V at low temperature T. The system is dilute so that the interparticle interactions are treated as perturbation in this case also and the deviation from the ideal behaviour is small.

We consider the Fermi gas at such densities and temperatures, where

$a/l \ll 1$ (low density)

$a/\lambda \ll 1$ (low temperature)

For a Fermi gas, however, these two assumptions are clearly related to each other.

We assume binary interaction between the particles. The Hamiltonian of the quantised field for fermions with spin 1/2 ($\sigma = \pm$ ½), is given by (10.6.34) viz.

$$\hat{H} = \sum_{P,\sigma} (P^2/2m)\, \hat{a}^+_{P\sigma}\hat{a}_{P\sigma} + (1/2) \sum u^{P_1'\sigma_1',\, P_2'\sigma_2'}_{P_1\sigma_1,\, P_2\sigma_2}\, \hat{a}^+_{P_1'\sigma_1'}\hat{a}^+_{P_2'\sigma_2'}\hat{a}_{P_2\sigma_2}\hat{a}_{P_1\sigma_1} \tag{10.9.1}$$

where $\hat{a}^+_{P\sigma}$ and $\hat{a}_{P\sigma}$ are the creation and annihilation operators for a free fermion with momentum **P** and spin σ. The summation of the second term of (10.9.1) is over all values of the momenta of a pair of particles, with the conditions which confirm the conservation laws of a momentum and spin. The matrix elements $u^{P_1'\sigma_1',\, P_2'\sigma_2'}_{P_1\sigma_1,\, P_2\sigma_2}$ are related to the scattering length a of binary collision through (10.7.6). At low temperature ($a/\lambda \ll 1$), as in case of bosons, the matrix elements in the sum of (10.9.1) can be replaced by their values at **P** = 0. Thus,

$$u^{P_1'\sigma_1',\, P_2'\sigma_2'}_{P_1\sigma_1,\, P_2\sigma_2} \quad u^{0\sigma_1',\, 0\sigma_2'}_{0\sigma_1,\, 0\sigma_2} \tag{10.9.2}$$

each of σ's has two values 1/2 and −1/2. Naturally, (10.9.2) contain a set of matrix elements with different values of σ's. However, we note that the fermion operators $\hat{a}_{P_1,\, \sigma_1}\hat{a}_{P_2\, \sigma_2}$ and $\hat{a}^+_{P_1\sigma_1'}\hat{a}^+_{P_2\sigma_2'}$

anticommute. Thus, all terms of the second sum of (10.9.1), which contain the same pair of indices σ_1, σ_2 or σ_1', σ_2' vanish. Thus, we write the Hamiltonian in the form

$$\hat{H} = \sum_{P,\sigma} (P^2/2m)\, \hat{a}^{+}_{P\sigma}\, \hat{a}_{P\,\sigma} + (u_0/V) \sum \hat{a}^{++}_{P_1'}\, \hat{a}^{+-}_{P_2}\, \hat{a}^{--}_{P_2'}\, \hat{a}^{+}_{P_2} \tag{10.9.3}$$

where

$$(u_0/V) = u^{0+,0-}_{0+,0-} - u^{0+,0-}_{0-,0+} \tag{10.9.4}$$

where the suffixes (+) and (-) denote $\sigma = 1/2$ and $\sigma = -1/2$, respectively. The summation in the second term of (10.9.3) goes over all values of momenta, with the condition

$$P_1 + P_2 = P_1' + P_2'$$

We apply the perturbation theory to evaluate the energy eigenvalues of the Hamiltonian (10.9.3). In this case, the perturbation theory is based on the concept that the main contribution arises from the ideal gas and the effect of interaction is small. Thus the Hamiltonian $\hat{H}$ of the Fermi gas can be written as

$$\hat{H} = \hat{H}_0 + \hat{H}_1 + \ldots \tag{10.9.5}$$

where $\hat{H}_0$ is the main term of $\hat{H}$, which is already diagonal. Thus,

$$\hat{H}_0 = \sum_{P,\sigma} (P^2/2m)\, \hat{a}^{+}_{P\sigma}\, \hat{a}_{P\,\sigma} \tag{10.9.6}$$

$\hat{H}_1$ is the first order correction, which is given by the matrix elements of the interaction energy, namely the elements for which $P_1' = P_1$ and $P_2' = P_2$. Thus,

$$\hat{H}_1 = (u_0/V) \sum_{P_1,P_2} \hat{a}^{++}_{P_1}\, \hat{a}^{+-}_{P_2}\, \hat{a}^{--}_{P_2}\, \hat{a}^{+}_{P_2}$$

$$= (u_0/V) \sum_{P_1,P_2} \hat{a}^{++}_{P_1}\, \hat{a}^{+-}_{P_1}\, \hat{a}^{+-}_{P_2}\, \hat{a}^{--}_{P_2} \tag{10.9.7}$$

The eigenvalues corresponding to the main term $\hat{H}_0$ of the Hamiltonian is

$$E^{(0)} = \sum_{P,\sigma} (P^2/2m) N_{P\sigma}$$

$$E^{(0)} = \sum_{P,\sigma} (P^2/2m)\, (N_P^{+} + N_P^{-}) \tag{10.9.8}$$

and the first order correction to the energy of the system is

$$E^{(1)} = (u_0/V) \sum_{P_1,P_2} N_{P_1}^{+}\, N_{P_2}^{-} \tag{10.9.9}$$

where $N_{P\sigma}$ is the occupation number of single-particle state $(\mathbf{P},\sigma)$. Its mean value is given by the Fermi distribution function

$$< N_{P\sigma}> = 1/(z_0^{-1} \exp(p/2mkT) + 1) \tag{10.9.10}$$

where

$$z_0 = \exp(\mu_0/kT)$$

is the fugacity of an ideal gas and μ_0 is its chemical potential. Replacing the sum of (10.9.8) by the integral, we get (see sec.8.2)

$$E^{(0)} = (4\pi V/h^3) \int_0^\infty \{(P^2/2m)/(z_0^{-1} \exp(P^2/2mkT)+1)\}\, P^2 dP$$

$$= 4\pi V\, (2m/h^2)^{3/2}\, F_{5/2}\,(z_0) \tag{10.9.11}$$

where

$$F_n(z_0) = \int_0^\infty \epsilon^{n-1} d\epsilon /(z_0^{-1} \exp(\epsilon/kT)+1)$$

with

$$\epsilon = (P^2/2m)$$

In order to evaluate z_0, we calculate the total number in the system, which is given by

$$N = \sum_{P,\sigma} N_{P\sigma} = (4\pi V/h^3) \int_0^\infty \{1/(z_0^{-1} \exp(P^2/2mkT)+1)\}\, P^2 dP$$

$$= 4\pi V\, (2m/h^2)^{3/2}\, F_{3/2}\,(z_0) \tag{10.9.12}$$

From (10.9.9), we have

$$N^+ = \sum_{P_1} N^+_{P_1}$$

$$N^- = \sum_{P_2} N^-_{P_2}$$

where N^+ and N^- denote the total number of particles with spin up and spin down, respectively. In case of equilibrium,

$$<N^+> = <N^-> = (1/2)N \tag{10.9.13}$$

Substituting these values in (10.9.9), we obtain the first order correction to the energy

$$E^{(1)} = (u_0/4V)N^2 = 4\pi^2 V u_0\, (2m/h^2)^3\, [F_{3/2}(z_0)]^2 \tag{10.9.14}$$

when u_0 is given by (10.7.9) viz,

$$u_0 = (4\pi a\hbar^2/m) \tag{10.9.15}$$

Adding (10.9.11) and (10.9.14), we obtain an expression for the energy in the first order correction

$$E_0 = E^{(0)} + E^{(1)} + \ldots$$

$$= 4\pi V (2m/h^2)^{3/2} [F_{3/2}(z_0) + \pi u_0 (2m/h^2)^{3/2} (F_{3/2}(z_0)^2 + \ldots] \tag{10.9.16}$$

In the low temperature limit, the function $F_n(z_0)$ can be evaluated as [see Eq.(8.2.18)]

$$F_n(z_0) = (1/n)\, \mu_0^n [1 + (\pi^2/6)\, n(n-1)\, (kT/\mu_0)^2 + \ldots] \tag{10.9.17}$$

where

$$\mu_0 = \epsilon_F [1 - (\pi^2/12)\, (kT/\epsilon_F) + \ldots] \tag{10.9.18}$$

Here ϵ_F is the Fermi energy, given by

$$\epsilon_F = (3\rho/8\pi)^{2/3}\, (\hbar^2/2m) \tag{10.9.19}$$

where $\rho = N/V$ is the number density. With the help of these equations, we get

$$F_{3/2}(z_0) = (2/3)\, \epsilon_F^{3/2} \tag{10.9.20}$$

$$F_{5/2}(z_0) = (2/5)\, \epsilon_F^{5/2} [1 + (5\pi^2/12)(kT/\epsilon_F)^2 + \ldots] \tag{10.9.21}$$

Substituting these values in (10.9.16), we obtain an expression for the ground state energy ($T \to 0$). Thus,

$$E_0 = (3/5)\, N\epsilon_F [1 + (5/12)(u_0\rho/\epsilon_F) + \ldots] \tag{10.9.22}$$

$$E_0/N = (3/5)\, \epsilon_F [1 + (5\pi/3)(\hbar^2/m)(a\rho/\epsilon_F) + \ldots]$$

$$= (3/10)\, (\hbar^2/m)\, (3\pi\rho)^{2/3} + (\pi a\hbar^2/m)\, \rho \tag{10.9.23}$$

The ground state pressure of the Fermi gas is then given by

$$P_0 = (\partial E_0/\partial V)_N = \rho^2\, (\partial(E_0/N)/\partial\rho)$$

$$= (1/5)\, (\hbar^2/m)\, (3\pi^2\rho)^{2/3}\rho + (\pi a\hbar^2/m)\, \rho^2$$

$$= (2/5)\, \rho\epsilon_F [\, 1 + (5/2)\, (\pi a\hbar^2/m)\, (\rho/\epsilon_F)] \tag{10.9.24}$$

The velocity of the sound wave C_0 of the gas is obtained using (10.7.40). Thus,

$$C_0^2 = (1/m)\, (\partial/\partial\rho)\, [\rho^2\, (\partial(E_0/N)/\partial\rho)] = (1/3)\, (\hbar^2/m^2)\, (3\pi^2\rho)^{2/3} + (\pi a\hbar^2/m^2)\, \rho$$
$$= (2/3)\, (\epsilon_F/m)\, [1 + (3\pi a\hbar^2/m)\, (\rho/\epsilon_F)] \tag{10.9.25}$$

The first terms of the foregoing expressions represent the ground state results for the ideal Fermi gas, and the second terms are the first order corrections to the ideal gas results which arise due to the deviation of imperfect Fermi gas from the ideal state.

Problems

10.1 Show that

$$W_2^{S/A}(1',2';1,2) = W_2(1',2';1,2) \pm W_2(2',1';1,2)$$

10.2 Using a plane wave function to describe the motion of a free particle, show that

$$U_2^{S/A}(1',2';1,2) = \pm W_1(2',1)\, W_1(1',2)$$

10.3 Calculate second virial coefficient for hard sphere gas of bosons/fermions at low temperature.

10.4 Calculate the leading quantum correction to the second virial coefficient of a hard sphere gas at high temperature.

10.5 What do you understand by an imperfect gas. Show that ground state energy for an imperfect Bose gas is

$$E_0/N = (2\pi a\hbar^2/m)\rho\,[1 + (128/15\pi^{1/2})(\rho a^3)^{1/2}]$$

10.6 Prove that following relation for a dilute Bose gas

(a) $P_0 = (2\pi a\hbar^2/m)\rho^2\,[1 + (64/5\pi^{1/2})(\rho a^3)^{1/2}]$

(b) $C_0^2 = (4\pi a\hbar^2/m^2)\rho\,[1 + (16/\pi^{1/2})(\rho a^3)^{1/2}]$

10.7 Show that the number density in the state with $P = 0$ is

$$\rho_0 = \rho\,[1 - (8/3\pi^{1/2})\,(\rho a^3)^{1/2}]$$

10.8 Show that the mean occupation number $\langle N_P \rangle$ of the real particles and the mean occupation number $\langle n_P \rangle$ of the quasi-particles of an imperfect Bose gas are related by the equation

$$\langle N(P) \rangle = (\langle n_P \rangle + \alpha_P^2(1+\langle n_P \rangle))/(1-\alpha_P^2) \qquad \text{for } \mathbf{P} \neq 0$$

which reduces to

$$\langle N(P) \rangle = \alpha_P^2/(1-\alpha_P^2) \qquad \text{for } \mathbf{P} = 0$$

10.9 Show that the energy of quasi-particle is

$$E(P) = (P^2/2m^*) + \rho_0 u_0$$

where m^* is the effective mass of a particle. Using this relation calculate the transition temperature. How does this transition temperature differs from that of an ideal Bose gas.

10.10 Show that the ground state energy of a Fermi gas is

$$E_0/N = (3/5)\,\epsilon_F\,[1 + (5\pi/3)(\hbar^2/m)(a\rho/\epsilon_F)]$$

10.11 Prove that for imperfect Fermi gas

(a) $P_0 = (2/5)\,\rho\epsilon_F\,[1 + (5/2)\,(\pi a\hbar^2/m)\,(\rho/\epsilon_F)]$

and

(b) $C_0^2 = (2/3)\,(\epsilon_F/m)\,[1 + (3\pi a\hbar^2/m)\,(\rho/\epsilon_F)]$

CHAPTER 11

THEORY OF DENSE GASES AND LIQUIDS

11.1. Introduction

In previous chapters, we have dealt with the dilute gases. In the present chapter, we consider the dense gases and liquids. Molecules in gases are distributed quite randomly in space. Molecules are moving with the amount of kinetic energy and attract each other with intermolecular forces. In case of dilute gases, the mean kinetic energy of the molecules is substantially greater than the mean interaction energy. Hence the molecules of a gas are almost completely disordered. When temperature is lowered the molecules comes closer to each other, and gases become dense. At low temperature the mean interaction energy will be larger than the mean kinetic energy and the motion of molecules will be controlled by interaction forces. The atoms (or molecules) of solids are arranged at quite definite points in space, which are called lattice sites. A liquid is midway between these two extremes. The molecules are close together (much like solid) so that the kinetic energy is sufficiently large to prevent the formation of an ordered (crystal) structure. Like a solid, a liquid is slightly compressible, like gas, it shows fluidity, lacking permanent rigidity. Due to fluidity, liquids and gases are referred as fluids.

As discussed in section 9.2, the thermodynamic properties of fluid are determinable from the cluster expansion of the configuration integral Z_N. However, the expansion series fail to coverage at high density, i.e., in case of dense gases and liquids. In this section we will discuss an alternative approach to calculate the thermodynamic properties of a dense fluid in terms of the radial distribution function (RDF) g(r).

11.2. Thermodynamic Properties

In this section, we derive the internal energy, pressure and compressibility of the system in terms of g(r).

1. Internal energy equation

The internal energy U is simplify the mean value <E> of the energy E and is given by (4.5.8) i.e.

$$U = kT^2 (\partial \ln Q_N/\partial T)_{N,V} \qquad (11.2.1)$$

where

$$Q_N = Z_N/N!\lambda^{3N} \qquad (11.2.2)$$

Substituting (11.2.2) in (11.2.1), we get

$$U = (3/2)\, NkT + U^{ex} \qquad (11.2.3)$$

where

$$U^{ex} = kT^2(\partial Z_N/\partial T)/Z_N \qquad (11.2.4)$$

If we assume the total potential to be pairwise additive, then Φ is the sum of $N(N-1)/2$ terms of $u(r_{ij})$, which gives the same integral. Thus,

$$U^{ex} = (N(N-1)/2Z_N) \int\int \exp[-\beta\Phi] u(r_{12}) \prod_{i=1}^{N} dr_i$$

$$= (1/2) \int\int u(r_{12}) [(N(N-1)/Z_N) \int\int \exp[-\beta\Phi] \prod_{i=3}^{N} dr_i] dr_1 dr_2$$

$$= (1/2) \rho^2 \int\int u(r_{12}) g(r_{12}) dr_1 dr_2 = (1/2) \rho^2 \int\int u(r_{12}) g(r_{12}) dr_1 dr_{12} \qquad (11.2.5)$$

where

$$\rho^2 g(r_{12}) = (N(N-1)/Z_N) \int \ldots \int \exp[-\beta\Phi] \prod_{i=3}^{N} dr_i \qquad (11.2.6)$$

Thus, the excess internal energy per particle is

$$U^{ex}/N = (1/2) \rho \int u(r) g(r) dr \qquad (11.2.7)$$

where $dr = dr_{12}$ and the integration is over all space. Using the spherical polar coordinates, the internal energy equation is

$$U/N = (3/2) kT + 2\pi\rho \int_0^{\infty} u(r) g(r) r^2 dr \qquad (11.2.8)$$

2. Virial pressure equation

The classical virial theorem of Clausius can be used to derive an expression for pressure. We consider a system of N identical particles, each of mass m. Let F_{x_i}, F_{y_i} and F_{z_i} be the components of the force F_i acting on the ith molecule; then the kinetic energy of the system is

$$K = \sum_i (p_i^2/2m) = \sum_i m\dot{r}_i^2 = (1/4) \sum_i m (d^2/dt^2) (r_i^2) - (1/2) \sum_i (\mathbf{r}_i.\mathbf{F}_i) \qquad (11.2.9)$$

where use has been made of the relation

$$(1/2) (d^2/dt^2) (r^2) \equiv (1/2) (d^2/dt^2) (\mathbf{r}.\mathbf{r}) = \dot{r}^2 + \mathbf{r}.\ddot{\mathbf{r}} \qquad (11.2.10)$$

Taking the average over a sufficiently long interval of time, τ, the first term vanishes in the case of steady state, i.e.

$$\langle (1/4) \sum_i m (d^2/dt^2) (r_i^2) \rangle_t = \lim_{\tau\to\infty} (1/\tau) \int_0^{\infty} (d/dt) ((1/2) \Sigma m \mathbf{r}_i.(d\mathbf{r}_i/dt)) dt$$

$$= \lim_{\tau\to\infty} (m/2\tau) \sum_i [(r_i (dr_i/dt))_{t=\tau} - (r_i (dr_i/dt))_{t=0}] \qquad (11.2.11)$$

and the time average of Eq.(11.2.9) becomes

$$\langle K \rangle = -(1/2) \langle \sum_i \mathbf{r}_i . \mathbf{F}_i \rangle \equiv X \tag{11.2.12}$$

This is the virial theorem of Clausius according to which the total kinetic energy of transition of the molecules of a system in the steady state is equal to its virial X. In Eq.(11.2.12) $\mathbf{F}_i$ is the total force acting on the ith particle. The virial can be written as a sum of two parts

$$X = X_e + X_{in} \tag{11.2.13}$$

where X_e is due to the external forces and X_{in} arises from the intermolecular forces. If the fluid is contained in a cubic box of length $L = V^{1/3}$ and P be the pressure exerted by the wall, then the virial of external force, like that of an ideal gas, is

$$X_e = (3/2)\, PV \tag{11.2.14}$$

The virial of the intermolecular force is given by

$$X_{in} = (1/2) \langle \sum_i \mathbf{r}_i . \nabla_i \Phi \rangle \tag{11.2.15}$$

Then the virial theorem is expressed in the form

$$\langle K \rangle \equiv \langle \sum_i p_i^2/2m \rangle = (3/2)\, PV + (1/2) \langle \sum_i \mathbf{r}_i . \nabla_i \Phi \rangle \tag{11.2.16}$$

or

$$PV = (2/3) \langle \sum_i p_i^2/2m \rangle - (1/3) \langle \sum_i \mathbf{r}_i . \nabla_i \Phi \rangle \tag{11.2.17}$$

Thus we obtain an expression for PV in terms of the total kinetic energy and intermolecular potential. We have taken the time averages. However, according to statistical mechanics, these time averages can be replaced by ensemble averages. In the canonical ensemble, the average $\langle f \rangle$ of any quantity f is given by

$$\langle f \rangle = (1/N!h^{3N} Q_N) \int f \exp[-\beta H_N] \prod_{i=1}^{N} d\mathbf{r}_i\, d\mathbf{p}_i \tag{11.2.18}$$

where H_N is the Hamiltonian of the system. Thus, we have

$$\langle \sum_i p_i^2/2m \rangle = (1/N!h^{3N} Q_N) \int (\sum_i p_i^2/2m) \exp[-\beta H_N] \prod_{i=1}^{N} d\mathbf{r}_i\, d\mathbf{p}_i = (3/2)\, NkT \tag{11.2.19}$$

and

$$\langle \sum_i \mathbf{r}_i . \nabla_i \Phi \rangle = (1/N!h^{3N} Q_N) \int (\sum_i \mathbf{r}_i . \nabla_i \Phi) \exp[-\beta H_N] \prod_{i=1}^{N} d\mathbf{r}_i\, d\mathbf{p}_i$$

$$= (1/Z_N) \int (\sum_i \mathbf{r}_i . \nabla_i \Phi) \exp[-\beta \Phi] \prod_{i=1}^{N} d\mathbf{r}_i$$

$$= (1/2) \int r_{12} (\partial u(r_{12})/\partial r_{12}) [(N(N-1)/Z_N) \int \exp(-\beta\Phi) \prod_{i=3}^{N} d\mathbf{r}_i]\, d\mathbf{r}_1 d\mathbf{r}_2$$

$$= (1/2)\,\rho^2 \int r_{12}\,(\partial u(r_{12})/\partial r_{12})\,g(r_{12})\,dr_1 dr_2$$

$$= (1/2)\,N\rho \int r_{12}\,(\partial u(r_{12})/\partial r_{12})\,g(r_{12})\,dr_{12} \qquad (11.2.20)$$

where

$$r_1.\nabla_1 u(r_{12}) + r_2.\nabla_2 u(r_{12}) = r_{12}\,(\partial u(r_{12})/\partial r_{12}) = r_{12}\,(\partial u(r_{12})/\partial r_{12})$$

Then the equation of state is given by

$$\beta P/\rho = 1 - (2\pi/3)\,\beta\rho \int_0^\infty r^3\,(\partial u(r)/\partial r)\,g(r)\,dr \qquad (11.2.21)$$

3. Compressibility equation

The isothermal compressibility K_T can be defined as

$$K_T = (1/\rho)\,(\partial\rho/\partial P)_{V,T} \qquad (11.2.22)$$

Using Eq.(5.3.9) and $\rho = \langle N\rangle/V$, we can write

$$kT\,(\partial\rho/\partial P)_{V,T} = (\partial\langle N\rangle/\partial \ln \Xi)_{V,T} = [z\,(\partial\langle N\rangle/\partial z)]_{V,T}/[z\,(\partial \ln \Xi/\partial z)]_{V,T} \qquad (11.2.23)$$

In the grand canonical ensemble, the average $\langle X\rangle$ of any quantity X, which does not depend on the coordinates and momenta, is given by

$$\langle X\rangle = \Xi^{-1} \sum_{N=0}^{\infty} (z^N X/N!) \int\int \exp[-\beta\Phi] \prod_{i=1}^{N} dr_i \qquad (11.2.24)$$

Thus, the mean number of particles is given by

$$\langle N\rangle = (1/\Xi) \sum_{N=0}^{\infty} (z^N N/N!) \int\int \exp[-\beta\Phi] \prod_{i=1}^{N} dr_i$$

$$= (1/\Xi)\,z(\partial\Xi/\partial z) = z\,(\partial \ln \Xi/\partial z) \qquad (11.2.25)$$

Differentiating it with respect to z, we obtain

$$z(\partial\langle N\rangle/\partial z) = (1/\Xi) \sum_{N=0}^{\infty} (z^N N^2/N!) \int\int \exp[-\beta\Phi] \prod_{i=1}^{N} dr_i - [(1/\Xi) \sum_{N=0}^{\infty} (z^N N/N!) \int\int \exp[-\beta\Phi] \prod_{i=1}^{N} dr_i]^2$$

$$= \langle N^2\rangle - \langle N\rangle^2 \qquad (11.2.26)$$

Then Eq.(11.2.23) becomes

$$kT\,(\partial\rho/\partial P)_{V,T} = [\langle N^2\rangle - \langle N\rangle^2]\,/\,\langle N\rangle \qquad (11.2.27)$$

Using the normalisation equation (5.4.15) for $n(r_1, \ldots, r_l)$

$$\int\int n(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_l) \prod_{i=1}^{l} d\mathbf{r}_i = \langle N!/(N-l)!\rangle \tag{11.2.28}$$

we have

$$\int n(\mathbf{r}_1,\mathbf{r}_2)\, d\mathbf{r}_1\, d\mathbf{r}_2 = \langle N(N-1)\rangle = \langle N^2\rangle - \langle N\rangle \tag{11.2.29}$$

and

$$\int n(\mathbf{r}_1)\, d\mathbf{r}_1 = \langle N\rangle \tag{11.2.30}$$

It, therefore, follows that

$$\langle N^2\rangle - \langle N\rangle^2 = \langle N\rangle + \int [n(\mathbf{r}_1,\mathbf{r}_2) - n(\mathbf{r}_1)n(\mathbf{r}_2)]\, d\mathbf{r}_1 d\mathbf{r}_2$$

$$= \langle N\rangle [1 + \rho \int (g(r) - 1)\, d\mathbf{r}] \tag{11.2.31}$$

From (11.2.27) and (11.2.31), we get

$$kT\, \rho\, K_T = kT\, (\partial\rho/\partial P)_{V,T} = 1 + \rho \int h(r)\, d\mathbf{r} \tag{11.2.32}$$

or

$$(1/kT)\, (\partial P/\partial\rho)_{V,T} = [1 + \rho \int h(r)\, d\mathbf{r}]^{-1} = 1 - \rho \int c(r)\, d\mathbf{r} \tag{11.2.33}$$

If exact results for g(r) are used then (11.2.8), (11.2.21) and (11.2.33) yield the same (exact) results for the thermodynamic properties of a fluid. However, it is necessary to introduce some approximations to calculate g(r); as a result, each of these equations yields different values of thermodynamic properties. In particular the virial pressure given by (11.2.21) may differ from the compressibility pressure obtained from (11.2.33).

11.3. Hard Sphere Fluid

Equation (11.2.21) can be used to calculate the pressure of the hard sphere fluid. From (9.7.21), the RDF g(r) can be expressed as

$$g(r) = y(r) \exp[-\beta u(r)] \tag{11.3.1}$$

Then (11.2.21) can be rewritten as

$$\beta P/\rho = 1 - (2\pi/3)\, \rho\beta \int_0^\infty r^3\, (\partial u(r)/\partial r) \exp[-\beta u(r)] y(r) dr \tag{11.3.2}$$

For hard sphere potential,

$$(\partial/\partial r) \exp[-\beta u(r)] = \delta(r - d)$$

where $\delta(r - d)$ is the Dirac δ– function. Then

$$\beta P/\rho = 1 + (2\pi/3)\, \rho \int_0^\infty r^3\, y(r)\, \delta(r - d)\, dr = 1 + (2\pi/3)\, \rho\, d^3\, g(d) \tag{11.3.3}$$

where we have used the fact that

$$g(d) = \lim_{r \to d} y(r) \tag{11.3.4}$$

Thus the pressure of the hard sphere fluid can be calculated from the value of the RDF at contact. Eq.(11.3.3) can be rewritten as

$$\beta P/\rho = 1 + 4\eta\, g(d) \tag{11.3.5}$$

where

$$\eta = (\pi/6)\, \rho\, d^3$$

is the packing fraction. Comparing (11.3.5) with (9.6.9), the RDF of the hard sphere fluid at the contact (i.e. at r=d) is given by

$$g(d) = (1 - (1/2)\eta)/(1 - \eta)^3 \tag{11.3.6}$$

The RDF can also be obtained from the structure factor, which is related to the RDF by the relation

$$S(k) = 1 + \rho \int \exp(-i\mathbf{k}.\mathbf{r})\, h(r)\, d\mathbf{r} \tag{11.3.7}$$

Conversely, h(r) can be expressed as the inverse Fourier transform of (S(k) – 1)

$$\rho h(r) = (1/(2\pi)^3) \int [S(k) - 1] \exp(-i\mathbf{k}.\mathbf{r})\, d\mathbf{k}$$

$$= (1/2\pi^2) \int [S(k) - 1]\, [\sin(kr)/kr]\, k^2\, dk \tag{11.3.8}$$

With the help of (11.2.32) and (11.3.7), it can be shown that the compressibility factor K_T is given by the relation

$$\rho kT\, K_T = 1 + \rho h(0) = S(0) \tag{11.3.9}$$

where S(0) is the value of S(k) for k = 0. The structure factor can be measured through the X-rays or neutron scattering experiments.

Thus, all the thermodynamic properties of a system can be determined from a knowledge of the RDF g(r).

11.4. Born Green Equation

The density expansion (9.7.14) of radial distribution function g(r) is useful only at low densities. This approach cannot be extended to liquid densities, since at liquid densities one has to consider several order terms of the series. Higher order terms will probably be completely inaccessible. In this section, we deal with approximate theories which relate the RDF to the pair potential.

One of the convenient approaches for constructing a theory for the distribution function is the Born-Green-Yvon (BGY) equation. A simple derivation of the BGY equation may be given as follows:

From (9.7.1), the RDF is given by

$$\rho^2 g(\mathbf{r}_1,\mathbf{r}_2) \equiv n_N(\mathbf{r}_1,\mathbf{r}_2) = (N(N-1)/Z_N) \int \ldots \int \exp[-\beta\Phi] \prod_{i=3}^{N} d\mathbf{r}_i \tag{11.4.1}$$

where

$$\Phi = \sum_{i<j} u(\mathbf{r}_i,\mathbf{r}_j) \tag{11.4.2}$$

is the total interaction potential. Differentiating (11.4.1) with respect to $\mathbf{r}_1$, we get

$$\nabla_1 n_N(\mathbf{r}_1,\mathbf{r}_2) = (N(N-1)/Z_N)\beta \int \ldots \int \nabla_i \Phi \exp[-\beta\Phi] \prod_{i=3}^{N} d\mathbf{r}_i \tag{11.4.3}$$

Using (11.4.2), we may write $\nabla_i \Phi$ as

$$\nabla_i \Phi = \nabla_1 \left(\sum_{i<j} u(\mathbf{r}_i,\mathbf{r}_j)\right) = \nabla_1 u(\mathbf{r}_1,\mathbf{r}_2) + \sum_{j=3}^{N} \nabla_1 u(\mathbf{r}_1,\mathbf{r}_j)$$

$$= \nabla_1 u(\mathbf{r}_1,\mathbf{r}_2) + (N-2)\,\nabla_1 u(\mathbf{r}_1,\mathbf{r}_3) \tag{11.4.4}$$

Substituting this value in (11.4.3), we obtain

$$\nabla_1 n_N(\mathbf{r}_1,\mathbf{r}_2) = -\beta(N(N-1)/Z_N) \int \ldots \int \nabla_1 u(\mathbf{r}_1,\mathbf{r}_2) \exp[-\beta\Phi] \prod_{i=3}^{N} d\mathbf{r}_i$$

$$-\beta(N(N-1)(N-2)/Z_N) \int \ldots \int \nabla_1 u(\mathbf{r}_1,\mathbf{r}_3) \exp[-\beta\Phi] \prod_{i=3}^{N} d\mathbf{r}_i$$

$$= -\beta \nabla_1 u(\mathbf{r}_1,\mathbf{r}_2) \{(N(N-1)/Z_N) \int \exp[-\beta\Phi] \prod_{i=3}^{N} d\mathbf{r}_i\}$$

$$-\beta \int d\mathbf{r}_3 \nabla_1 u(\mathbf{r}_1,\mathbf{r}_3) \{(N(N-1)(N-2)/Z_N) \int \ldots \int \exp[-\beta\Phi] \prod_{i=4}^{N} d\mathbf{r}_i\}$$

With the help of (9.7.1), it can be written as

$$\nabla_1 n_N(\mathbf{r}_1,\mathbf{r}_2) = -\beta \nabla_1 u(\mathbf{r}_1,\mathbf{r}_2)\, n_N(\mathbf{r}_1,\mathbf{r}_2) - \beta \int d\mathbf{r}_3 \nabla_1 u(\mathbf{r}_1,\mathbf{r}_3)\, n_N(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) \tag{11.4.5}$$

or

$$-kT\, \nabla_1 g(\mathbf{r}_1,\mathbf{r}_2) = g(\mathbf{r}_1,\mathbf{r}_2)\, \nabla_1 u(\mathbf{r}_1,\mathbf{r}_2) + \rho \int \nabla_1 u(\mathbf{r}_1,\mathbf{r}_3)\, g(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) d\mathbf{r}_3 \tag{11.4.6}$$

where ∇_1 denotes the gradient operator at $\mathbf{r}_i$. Eq.(11.4.6) is the second equation of the BGY hierarchy and has been extensively used to study the structure of fluid. The equation relates $g(\mathbf{r}_1,\mathbf{r}_2)$ to the pair potential $u(\mathbf{r}_1,\mathbf{r}_2)$ only through another unknown function $g(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)$. This expression, though exact, can not be solved for $g(\mathbf{r}_1,\mathbf{r}_2)$, unless $g(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)$ is approximated. The superposition approximation, proposed by Kirkwood (1935) may be written as

$$g(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) = g(\mathbf{r}_1,\mathbf{r}_2)\, g(\mathbf{r}_1,\mathbf{r}_3)\, g(\mathbf{r}_2,\mathbf{r}_3) \tag{11.4.7}$$

which is commonly known as Kirkwood superposition approximation. When used, it enables us to write the BGY theory in a closed form as

$$-kT\, \nabla_1 \ln g(\mathbf{r}_1,\mathbf{r}_2) = \nabla_1 u(\mathbf{r}_1,\mathbf{r}_2) + \rho \int \nabla_1 u(\mathbf{r}_1,\mathbf{r}_3)\, g(\mathbf{r}_1,\mathbf{r}_3)\, g(\mathbf{r}_2,\mathbf{r}_3) d\mathbf{r}_3 \tag{11.4.8}$$

This equation can be solved subject to the boundary condition

$$g(r_1,r_2) \to 1, \; r_{12} \to \infty.$$

This is a non-linear intergo-differential equation, relating the RDF g(r) to the pair potential u(r) and is solved numerically by interactive method. The BGY theory is found to be less satisfactory quantitatively than other theories.

11.5. Integral Equations

The Ornstein-Zernike(OZ) equation (9.7.10) is the starting point for most integral equation studies of fluids. This equation is exact. The other equation is the closure relation

$$c = c[h] \tag{11.5.1}$$

and is in approximation.

Two integral equation approximations for fluids are the Percus-Yevick(PY) and hypernetted chain (HNC) approximation. The closure relations under the PY and HNC approximations are given as

$$c_{PY}(r_1,r_2) = f(r_1,r_2)\, Y(r_1,r_2) = (1 - \exp[\beta u(r_1,r_2)])\, g(r_1,r_2) \tag{11.5.2}$$

and

$$c_{HNC}(r_1,r_2) = f(r_1,r_2)\, Y(r_1,r_2) + [Y(r_1,r_2) - 1 - \ln Y(r_1,r_2)]$$

$$= h(r_1,r_2) - \ln g(r_1,r_2) - \beta u(r_1,r_2) \tag{11.5.3}$$

where

$$f(r_1,r_2) = \exp[-\beta u(r_1,r_2)] - 1 \tag{11.5.4}$$

is the two- particle Mayer function and

$$Y(r_1,r_2) = g(r_1,r_2) \exp[\beta u(r_1,r_2)] \tag{11.5.5}$$

A comparision of (11.5.2) and (11.5.3) gives

$$c_{HNC}(r_1,r_2) - c_{PY}(r_1,r_2) = Y(r_1,r_2) - 1 - \ln Y(r_1,r_2) \tag{11.5.6}$$

This shows that the PY-approximation is more drastic than the HNC approximation in terms of set of diagrams neglected. In spite of this, the PY-approximation is found to be superior when the repulsive potentials are dominant.

Substituting (11.5.2) in the OZ equation(9.7.10), we get the PY integral equation

$$g_{PY}(r_1,r_2) = \exp[-\beta u(r_1,r_2)]\,[1 + \rho \int (1 - \exp[\beta u(r_1,r_3)]) g(r_1,r_3)\,[g(r_2,r_3) - 1]dr_3 \tag{11.5.7}$$

where as substitution of (11.5.3) in (9.7.11) leads to the HNC integral equation

$$\ln g_{HNC}(r_1,r_2) = -\beta u(r_1,r_2) + \rho \int [g(r_1,r_3) - 1 - \ln g(r_1,r_3) - \beta u(r_1,r_3)]\,[g(r_2,r_3) - 1]dr_3 \tag{11.5.8}$$

These are non-linear integral equation for g, which are solved numerically.

A considerable amount of work has been done on the PY and HNC theories for hard sphere and Lennard Jones (12-6) system. The PY theory works well for hard spheres. The HNC theory had proven to be superior to both the PY and BGY theories for the Lennard-Jones(12-6) fluids.

11.6. Perturbation Theory

A perturbation theory has proved very useful tool in understanding the properties of fluids. The basic idea of this theory is to divide the pair potential into two parts; one part is regarded as a reference potential and other as a perturbation. In particular, the pair potential is written as

$$u(r) = u_0(r) + \xi\, u_1(r) \tag{11.6.1}$$

where $u_0(r)$ is the unperturbed or reference potential and $u_1(r)$ is the perturbation. When $\xi = 0$, (11.6.1) represents the pair potential of the reference system and when $\xi = 1$, (11.6.1) is the pair potential of the actual system. In (11.6.1), ξ characterizes the strength of the parameter and set equal to unity in the final results.

Substituting (11.6.1) in (9.1.4), the logarithm of the configuration integral is given by

$$\ln Z_N(V,T,\xi) = \ln \int \dots \int \exp\left[-\beta \sum_{i<j} \{u_0(r_{ij}) + \xi u_1(r_{ij})\}\right] \prod_{i=1}^{N} d\mathbf{r}_i \tag{11.6.2}$$

We now expand (11.6.2) in powers of ξ

$$\ln Z_N(V,T,\xi) = \ln Z_N(V,T,0) + [\xi(\partial/\partial\xi)\ln Z_N(V,T,\xi)]_{\xi=0} + 0(\xi^2) \tag{11.6.2'}$$

where

$$[\xi(\partial/\partial\xi)\ln Z_N(V,T,\xi)]_{\xi=0} = -\beta(N(N-1)/2Z_N(V,T,0)) \int\int \exp\left[-\beta \sum_{i<j} u_0(r_{ij})\right] u_1(r_{12}) \prod_{i=1}^{N} d\mathbf{r}_i$$

$$= -(\beta/2) \int u_1(r_{12}) \{(N(N-1)/Z_N(V,T,0)) \iint \exp[-\beta \sum_{i<j} u_0(r_{ij})] \prod_{i=3}^{N} \} d\mathbf{r}_1 d\mathbf{r}_2$$

$$= -(\beta/2)\, \rho^2 \int u_1(r_{12})\, g_0(r_{12})\, d\mathbf{r}_1 d\mathbf{r}_2$$

$$= (1/2)\, \beta N \rho \int u_1(r_{12}) g_0(r_{12}) d\mathbf{r}_{12} \tag{11.6.4}$$

Using the relation

$$A = kT \ln Q_N = -kT \ln (Z_N/N!\lambda^{3N}) \tag{11.6.5}$$

the expression for the Helmholtz free energy is given by

$$A(V,T) = A_0(V,T) - (1/2)\, N\rho \int u_1(r)\, g_0(r)\, d\mathbf{r} \tag{11.6.6}$$

where A_0 and $g_0(r)$ are, respectively, the Helmholtz free energy and RDF of the reference system (i.e. of the system for ξ=0). The higher order terms can be similarly expressed as integrals of three and higher particle distribution functions of the reference system.

As the properties of the hard sphere system are well known accurately, one would like to take hard spheres as the reference system.

This approach can be applied to a system, whose molecules interact via a hard-core plus attractive tail potential such as the square well model.

The approach can be extended to a real system provided the hard sphere diameter is known. Barker and Henderson (1967) have a method of achieving this goal. According to the Barker-Henderson theory

$$u_0(r) = u(r) \quad , r < \sigma$$

$$= 0 \quad , r > \sigma \qquad (11.6.7a)$$

and

$$u_1(r) = 0 \quad , r < \sigma$$

$$= u(r) \quad , r > \sigma \qquad (11.6.7b)$$

where u(r) is the Lennard-Jones(12-6) potential (Eq.9.4.11). Then the hard sphere diameter d is given by

$$d = \int_0^\sigma (1 - \exp[-\beta u_0(r)])\, dr \qquad (11.6.8)$$

which is temperature dependent and accounts for the 'softnen' of $u_0(r)$. Then A_0 and $g_0(r)$ may be approximated by

$$A_0 = A_{HS} \qquad (11.6.9a)$$

and

$$g_0(r) = g_{HS}(r) \qquad (11.6.9b)$$

Finally Eq.(11.6.6) can be expressed in the final form

$$\beta A/N = (\beta A_{HS}/N) - 2\pi\rho\beta \int_\sigma^\infty u_1(r)\, g_{HS}(r)\, r^2\, dr \qquad (11.6.10)$$

where A_{HS} is the Helhmholtz free energy of the hard sphere fluid and given by (9.6.10). The second term of (11.6.10) is the first order perturbation correction to the free energy. This can be solved numerically provided values of $g_{HS}(r)$ are available. (11.6.10) has been tested and found to very accurate.

Table 11.1. The equation of state $\beta P/\rho$ for the Lennard Jones (12-6) fluid

kT/ϵ	$\rho\sigma^3$	BH	Exact
2.72	0.65	2.24	2.22
	0.85	4.48	4.38
	0.95	6.41	6.15
1.35	0.50	0.31	0.30
	0.85	3.54	3.37
	0.95	6.21	6.32
1.00	0.65	-0.21	-0.25
	0.85	2.48	2.25

The perturbation theory is applied to the Lennard-Jones(12-6) fluid. The results from the Barker-Henderson(BH) perturbation theory for the equation of state of the Lennard Jones (12-6) fluid are compared with the exact simulation result in Table 11.1. The agreement is good. Different schemes have been proposed for the division of the potential. The Barker Henderson (BH)and Weeks-Chandler Anderson (WCA) theories are the most satisfactory theories for the equilibrium properties of fluids. They are comparable in accuracy. For detail, the readers are referred to Barker and Henderson (1976) and Hansen and McDonald (1986).

11.7. Quantum Mechanical Hard Sphere Fluid

In this section, we consider a quantum mechanical fluid of hard sphere at high temperature, where the quantum effects are small and can be treated as a correction to the classical system. Usual way of studying the properties of fluids is to expand them in power of $\hbar$. The first term of this series is a classical value and other terms arise due to the quantum effects.

Substituting (10.4.5) in (4.9.6), we get

$$Q_N = (1/N!\lambda^{3N}) \int\!\!\ldots\!\int W_N^C(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)\,[1 + \sum_{i<j} U_2^m(\mathbf{r}_i,\mathbf{r}_j) + \ldots] \prod_{i=1}^{N} d\mathbf{r}_i$$

$$= (1/N!\lambda^{3N}) \int\!\!\ldots\!\int W_N^C(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)\,[1 + (N(N-1)/2)U_2^m(\mathbf{r}_1,\mathbf{r}_2) + \ldots] \prod_{i=1}^{N} d\mathbf{r}_i$$

$$= Q_N^C [1 + (1/2) \int\int U_2^m(\mathbf{r}_1,\mathbf{r}_2)\,\{(N(N-1)/N!\,\lambda^{3N}Q_N^C) \int\!\!\int W_N^C(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N) \prod_{i=1}^{N} d\mathbf{r}_i\}\, d\mathbf{r}_1 d\mathbf{r}_2]$$

$$= Q_N^C [1 + (1/2)\,\rho^2 \int\int U_2^m(\mathbf{r}_1,\mathbf{r}_2)\, g^C(\mathbf{r}_1,\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2] \qquad (11.7.1)$$

where

$$\rho^2 g^C(\mathbf{r}_1,\mathbf{r}_2) = (N(N-1)/N!\lambda^{3N}Q_N^C) \int\!\!\ldots\!\int W_N^C(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N) \prod_{i=3}^{N} d\mathbf{r}_i \qquad (11.7.2)$$

and

$$Q_N^C = (1/N!\lambda^{3N}) \int\!\!\ldots\!\int W_N^C(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N) \prod_{i=1}^{N} d\mathbf{r}_i \qquad (11.7.3)$$

Here $g^C(\mathbf{r}_1,\mathbf{r}_2)$ is the RDF of the classical fluid and Q_N^C is its classical partition function.

Using the relation (11.5.5) i.e

$$A = -kT \ln Q_N \qquad (11.7.4)$$

We get the expression for the Helmholtz free energy

$$\beta A/N = (\beta A^C/N) - (1/2)\,\rho \int g^C(\mathbf{r}_{12})\, U_2^m(\mathbf{r}_{12})\, d\mathbf{r}_{12} + 0(\lambda^2) \qquad (11.7.5)$$

Other thermodynamic properties can be obtained from (11.7.5). Thus the expression for pressure is given by

$$\beta P/\rho = (\beta P^C/\rho) - (1/2)\,\rho \int (\partial/\partial\rho)[\rho g^C(\mathbf{r}_{12})]\, U_2^m(\mathbf{r}_{12})\, d\mathbf{r}_{12} + 0(\lambda^2) \qquad (11.7.6)$$

Here A^C and P^C are respectively, the Helmholtz free energy and pressure of the classical hard sphered fluid and U_2^m is the modified Ursell function given by (10.4.10).

Substituting (10.4.10) in (11.7.5), we immediately get

$$\beta A/N = (\beta A^C/N) + A^1(\lambda/d) \tag{11.7.7}$$

where

$$A^1 = 2^{-1/2}\,\pi(\rho d^2)\,g^C(d) \tag{11.7.8}$$

Similarly from (11.7.6), we get

$$\beta P/\rho = (\beta P^C/\rho) + P^1(\lambda/d) \tag{11.7.9}$$

where

$$P^1 = 2^{-1/2}\,\pi(\rho d^3)\,(\partial/\partial(\rho d^3))\,[(\rho d^3)g^C(d)] \tag{11.7.10}$$

From (9.6.10) and (9.6.9), we have

$$\beta A^C/N = \eta(4-3\eta)/(1-\eta)^2 \tag{11.7.11}$$

and

$$\beta P^C/\rho = 1 + 4\eta g(d)\,(1 + \eta + \eta^2 - \eta^3)\,/\,(1-\eta)^3 \tag{11.7.12}$$

giving

$$g(d) = (1 - (1/2)\eta)\,/\,(1-\eta)^3 \tag{11.7.13}$$

where $\eta = \pi\rho d^3/6$.

Using (11.7.11) - (11.7.13), the expressions for the free energy and pressure, correct to the first order in λ are given by

$$\beta A/N = (\eta/(1-\eta)^2)\,[(4-3\eta) + 3\sqrt{2}\,\{(1-(1/2)\eta)/(1-\eta)\}\,(\lambda/d)] \tag{11.7.14}$$

and

$$\beta P/\rho = (1/(1-\eta)^3)\,[(1+\eta+\eta^2-\eta^3)+3\sqrt{2}\eta\{(1+\eta-(1/2)\eta^2)/(1-\eta)\}(\lambda/d)] \tag{11.7.15}$$

The above equations can be rewritten as

$$\beta A/N = [1 + 2^{-3/2}\,\lambda\,(\partial/\partial d)]\,(\beta A^C/N) \tag{11.7.16}$$

and

$$\beta P/\rho = [1 + 2^{-3/2}\,\lambda\,(\partial/\partial d)]\,(\beta P^C/\rho) \tag{11.7.17}$$

Thus, the first order quantum correction to the thermodynamic properties of a hard sphere fluid can be obtained by replacing the actual diameter d by an effective diameter $(d+2^{-3/2}\lambda)$.

Table 11.2: Values of A^1 and P^1 for the hard sphere fluid.

ρd^3	A^1	P^1
0.3	1.025	1.511
0.6	3.483	7.619
0.8	7.159	20.744

The quantum coefficients A^1 and P^1 are given in Table 11.2 for $\rho d^3 = 0.3$, 0.6 and 0.8. From the Table we see that the first quantum correction to the free energy and pressure is appreciable at all densities and increases with density.

11.8. Quantum Correction for Fluid of Analytic Potential

For an analytic potential, the Slater sum of the system is given by Eq.(10.4.26). Substituting this value in Eq.(4.9.6), the partition function can be written as

$$Q_N = (1/N!\lambda^{3N}) \int\int \exp[-\beta U] [1 + (\hbar^2\beta^2/12m) \sum_i \{-\nabla_i^2 U + (1/2)\beta(\nabla_i U)^2\}] \prod_{i=1}^{N} d\mathbf{r}_i \qquad (11.8.1)$$

Integrating by parts, it can be shown that

$$\int \exp[-\beta U] \nabla_i^2 U \, d\mathbf{r}_i = \exp[-\beta U] \nabla_i U + \beta \int \exp[-\beta U] (\nabla_i U)^2 d\mathbf{r}_i$$

$$= \beta \int \exp[-\beta U] (\nabla_i U)^2 d\mathbf{r}_i \qquad (11.8.2)$$

where the contribution of the first term is neglected. Then (11.8.1) can be expressed in the form

$$Q_N = Q_N^C [1 - (\hbar^2\beta^2/24m) \sum_i <(\nabla_i^2 U)>] \qquad (11.8.3)$$

where Q_N^C is the classical partition function and $<\nabla_i^2 U>$ is the mean value defined by

$$\sum_i <\nabla_i^2 U> = [\int\ldots\int \exp[-\beta U] \sum_i (\nabla_i^2 U) \prod_{i=1}^{N} d\mathbf{r}_i] / Z_N^C \qquad (11.8.4)$$

Assuming the total potential energy U as the pair wise additive, (11.8.4) can be written as

$$\sum_i <\nabla_i^2 U> = (N(N-1)/2Z_N^C) \int\ldots\int \exp[-\beta U] \nabla^2 u(r_{12}) \prod_{i=1}^{N} d\mathbf{r}_i$$

$$= (1/2) N\rho \int g^c(r_{12}) \nabla^2 u(r_{12}) \, d\mathbf{r}_{12} \qquad (11.8.5)$$

where $g^c(r_{12})$ is the RDF of the classical fluid.

Using the relation

$$A = -kT \ln Q_N$$

the Helmholtz free energy is given by

$$\beta A/N = (\beta A^C/N) + (\hbar^2\beta^2/24m) \rho \int g^C(\mathbf{r}_{12}) \nabla^2 u(r_{12}) \, d\mathbf{r}_{12} \qquad (11.8.6)$$

where A^C is the classical Helmholtz free energy and the first order correction to it is proportional to $\hbar^2$.Eq.(11.8.6) can be written as

$$\beta A/N = (\beta A^C/N) + (\beta A^1/N) \qquad (11.8.7)$$

where

$$\beta A^1/N = (\hbar^2\beta^2/24m) \rho \int g^C(\mathbf{r}_{12}) \nabla^2 u(r_{12}) \, d\mathbf{r}_{12} \qquad (11.8.8)$$

Then the pressure and the internal energy are

$$\beta P/\rho = (\beta P^C/\rho) + (\beta P^I/\rho) \tag{11.8.9}$$

where

$$\beta P^I/\rho = (\hbar^2\beta^2/24m)\,\rho \int [g^C(\mathbf{r}_{12}) + \rho\, \partial g^C(\mathbf{r}_{12})/\partial\rho\,]\, \nabla^2 u(r_{12})\, d\mathbf{r}_{12} \tag{11.8.10}$$

and

$$\beta U/N = (\beta U^C/N) + (\beta U^I/N) \tag{11.8.11}$$

where

$$\beta U^I/N = (\hbar^2\beta^2/24m)\,\rho \int [g^C(\mathbf{r}_{12}) + \beta\, \partial g^C(\mathbf{r}_{12})/\partial\beta\,]\, \nabla^2 u(r_{12})\, d\mathbf{r}_{12} \tag{11.8.12}$$

It is clear from these expressions that the quantum correction to the classical value is always positive and increases with decrease of atomic mass and temperature.

Eqs.(11.8.6)-(11.8.8) can be used to calculate the first order quantum correction to the thermodynamic properties of the Lennard-Jones (12-6) fluids such as neon.

The first order quantum correction to the free energy A for neon is shown in Table 11.3, at two states, $\rho^* = 0.726$, $T^* = 0.950$ and $\rho^* = 0.808$, $T^* = 0.665$, where $\rho^* = \rho\sigma^3$ is the reduced density and $T^* = kT/\epsilon$ reduced temperature. At these states the quantum effects are significant.

Table 11.3. Values of the first order quantum correction to the free energy A^C for neon.

$\rho\sigma^3$	kT/ϵ	$\beta A^I/N$
0.726	0.950	0.244
0.808	0.665	0.370

11.9. Liquid Crystals

Liquid crystal is a state of matter intermediate between that of crystalline solid and isotropic liquid. For many substances, especially organic materials, we can not treat the transition from the solid to the liquid state as a single transition. For such materials this transition consists of a sequence of transitions in each of which the state and structure of the substance change. It is impossible to state that it is either in the solid or in the liquid state. It combines the properties of both phases. A substance in the intermediate states is called liquid crystal.

11.9.1 Types of liquid crystals

Liquid crystals exhibit an ordering which is intermediate between these of solids and liquids and which results in corresponding anisotropy of their properties. Accordingly, liquid crystals are classified broadly into three types: nematic, cholesteric and smectic.

Fig.1.1. Orientational order of molecules in a nematic

(i) **Nematics** : These liquid crystals have a high degree of long range orientational order of molecules, but no long range translational order (Fig.11.1). These liquid crystals do not have a spatial ordering. Molecules in the nematic liquid crystal are spontaneously oriented with their long axes approximately parallel. Thus it differs from the isotropic liquid. The line of orientation of nematic molecules serves as a preferred direction. This line is the symmetry axis for the properties of the nematic, the two directions along this line being equivalent. If the molecules possess a dipole moment, the orientation of dipoles in these two directions is equally probable. The dipole moments of one half of molecules are oriented in one direction, and of the other half in opposite direction. For this reason, a nematic is optically uniaxial, positive and strongly birefringent. Nematic liquid crystals can be found only among the materials in which the right and left handed forms of molecules coincide.

(ii) **Cholesterics** : The cholesteric liquid crystal is also a nematic type of liquid crystal except that it is composed of optically active molecules. If an excess of right- or left- handed molecules are created in a nematic, the structure of the nematic phase is distorted and spiral type distortion appears in the structure. This type of distortion is seen, in particular, for a pure ester of cholestrol. Hence a spiral phase appearing here is called cholesteric. In this case just for the nematic phase the local properties in each region are characterized by the direction of orientation of molecules in it. However, in contrast to

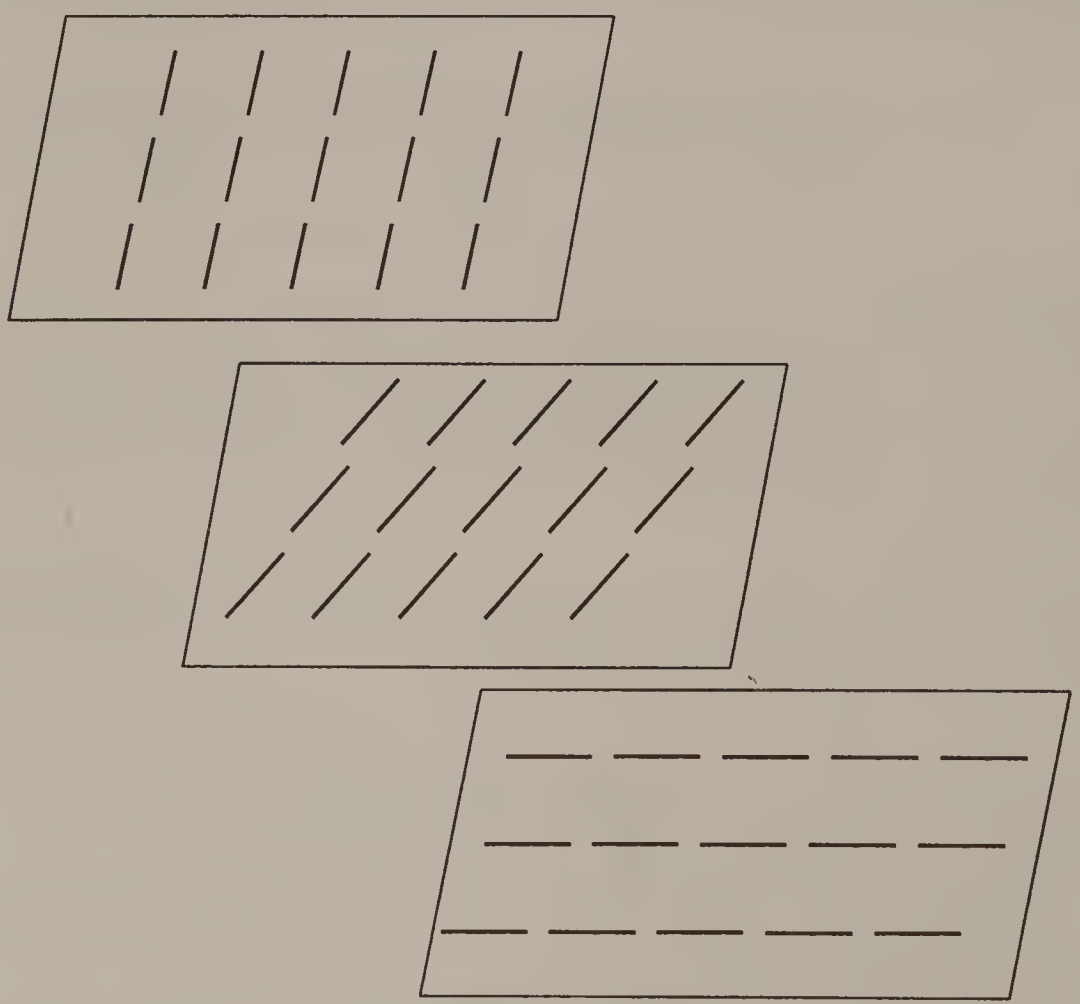


Fig.11.2. Representation of a cholesteric liquid crystal

the nematic phase, the direction of preferential orientation changes upon transition from one region to another, as a result of which a helical structure appears (Fig.11.2). The spirals can have right handed as well as left handed rotation. This depends on the type of molecules in excess.

(iii) **Smectics**: Smectic liquid crystals have stratified structures but a variety of molecular arrangements are possible within each stratification. There are three types of smectics denoted by A, B and C. In smectic A the molecules are upright in each layer with their centres irregularly spaced in a liquid-like fashion (Fig.11.3a). The thickness of the layers in A-type smectics is closed to the length of molecules directed on average perpendicularly to the boundary surface between the layers. The local properties of the system of layers are axially symmetric with respect to the rotation axis. The rotation axis is normal to the boundary surface between the layers, both directions of the normal being equivalent. The layers are able to slide over each other relatively easily. Thus this liquid crystals has fluid properties, though it is very viscous than the nematic phase. Smectic B differs from A in that the molecular centres in each layer are hexagonal closed packed.

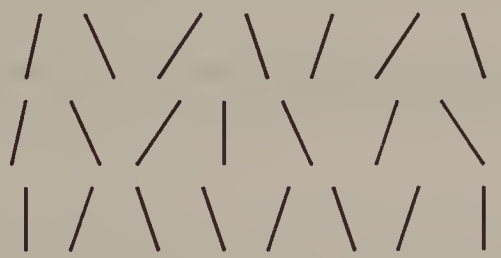


Fig.11.3a. Structure of Sematic A

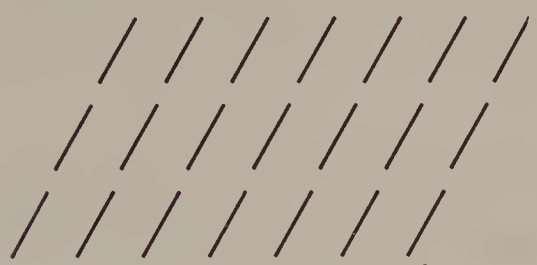


Fig.11.3b. Structure of Smectic C.

Smectic C is a tilted form of smectic A, i.e. the molecules are inclined with respect to layers (Fig.11.3b). In A- and C- types smectics, the layers of liquid behave as a two-dimensional liquid. In B type smectics, the layers of liquid are closer in their properties to a two- dimensional solid. Within the layers, periodicity and rigidity are observed. The layers of A- and C- type smectics are curved while those of the B- type smectic are flat.

From optical point of view, A- type smectics exhibit the properties of uniaxial crystal and C-type smectics have properties of typical of biaxial crystal. If long molecules forming a C-type smectics are optically active, and if the number of left- and right- hand types of molecules are not the same, the smectics becomes very complicated.

In addition to A-, B- and C- types smectics, there are some other types (H, D, E, ...), which will not be considered in this chapter.

11.9.2. Phase transition in molecular crystals

We consider molecular crystals composed of long narrow molecules. In the solid state these molecules are more or less parallel. On heating transformation takes place from the solid to the nematic phase. This transformation from the solid to the nematic phase is characterized by the break down of the positional order of molecules, but not the orientational order. The liquid crystal is fluid as well as anisotropic because the ability with which the molecules slide over one another without changing their parallelism. On further heating degree of orientational order in the liquid crystal decreases gradually. Some thermodynamic properties, such as specific heat, thermal expansion and isothermal compressibility, increase rapidly as the temperature approaches the nematic-isotropic point T_{NI}. At T_{NI} a first order (discontinuous) phase transition takes place, accompanied by the complete breakdown of the long range orientational order.

$$\text{Solid} \xleftarrow[T_1]{\text{heating}} \text{nematic} \xleftarrow[T_2]{\text{heating}} \text{isotropic}$$

Some typical examples of mesophase transitions in thermotropic materials are given below. All the transitions listed here take place reversibly on heating and cooling.

(i) P-azoxyanisole

$$\text{Solid} \xleftarrow{118.2\ C} \text{nematic} \xleftarrow{135.3\ C} \text{isotropic}$$

(ii) Cholesteryl benzoate

$$\text{Solid} \xleftarrow{147\ C} \text{nematic} \xleftarrow{186\ C} \text{isotropic}$$

(iii) Ethyl P-azoxycinnamate

$$\text{Solid} \xleftarrow{140\ C} \text{Smectic A} \xleftarrow{250\ C} \text{isotropic}$$

11.9.3. The Landau-de Gennes theory of liquid crystals

Many attempts have been made to develop the theory of liquid crystals. One is the phenomenological theory of Landau and deGennes, in which the Helmholtz free enrgy is expanded in power of the order parameters and its gradient.

The Helmholtz free enerrgy of any ordered system depends on a scalar order parameter S, defined as

$$S = (1/2) < 3 \cos^2\theta - 1 > \qquad (11.9.1)$$

where θ is the angle which the long molecular axis makes with orientational direction **n**, and the angular bracket denote the statistical average. The parameter S is known as long range orientational parameter in the nematic phase. For perfectly parallel alignment S=1, while for random orientation S=0. In the nematic phase S has an intermediate value which is strongly temperature dependent. The excess helmholtz free energy of an ordered system can be expanded in the form

$$F = (1/2)AS^2 - (1/3)BS^3 + (1/4)\,CS^4 + \ldots \qquad (11.9.2)$$

where $B > 0$ and $C > 0$. It is found that such an expression predicts a discontinuous transition. At the transition point T_c, we put

$$F = 0 \qquad (11.9.3a)$$

and

$$\partial F/\partial S = 0 \qquad (11.9.3b)$$

Using the conditions, we get the value of S at T_C

$$S_C = 2B/3C \qquad (11.9.4)$$

where higher order terms are neglected.
Using (11.9.4) in (11.9.2), we get

$$A = 2B^2/9C \qquad (11.9.5)$$

If $B = 0$, the transition is continuous and A becomes zero at the transition point. In the disordered phase $S = 0$, which corresponds to a minimum of F only $A < 0$. On the other hand in the ordered phase $S \neq 0$, which corresponds to a stable minimum only if $A > 0$. Then A is positive on one side of the transition point and negative on the other side and vanishes at the transition point.

In the vicinity of the transition, we may write

$$A = a\,(T - T^*) \qquad (11.9.6)$$

where T^* is the second order transition temperature. In case of a ferromagnet, T^* is the Curie temperature. If $B > 0$,

$$T_C - T^* = A/a = 2B^2/9C \qquad (11.9.7)$$

Thus T^* lies below T_C. For a 'weak' first order transition, B is small and hence $(T_C\text{-}T^*)$ may be very small quantity.

In principle, a free energy expansion of this type will be valid for nematic liquid crystals with the usual orientational parameter S defined by (11.9.1). However, in the nematic phase, S is usually quite large (greater than about 0.4), so that more terms are needed in the expansion in order to draw any definite conclusions. Consequently, the Landau – deGennes theory is conveniently applied only to the weakly ordered isotropic phase.

This theory is physically appealing and mathematically convenient. However it suffers from many drawbacks, for example, lack of quantitative power about phase diagram.

11.9.4. Properties and applications of liquid crystals

Liquid crystals have very important optical properties. Nematic and smectic A are uniaxial crystals, whose properties readily change under external effect over a wide range. These properties have a wide application and aroused an interest towards their investigation. Liquid crystals are used to control the light flow.

Cholesterics have helical periodicity in their structure, due to this structure, they exhibit diffraction properties in the visible region of the spectrum. The pitch of a helix changes under the action of external factor such as temperature. These external effects can also be used to control the light flow.

Electric and magnetic field produce a strong effect on the properties of liquid crystals. At present, the investigation of these effects has become a subject of active scientific research. The results of investigation are of practical utility. Digital indications (display) based on liquid crystals are well known. A method has been developed for obtaining visual image in microwave radiation. The advantages of liquid crystal films are their comparatively low cost and low electric power consumption. Thus liquid crystals have wide applications and are very useful at the present time.

Problems

11.1 Show how the internal energy, entropy and pressure can be calculated from the partition function.

11.2 Derive expressions for the internal energy and pressure in terms of the radial distribution function.

11.3 Show that the radial distribution function of a hard sphere fluid at the contact is
$g(d) = (1 - (1/2)\eta) / (1-\eta)^3$
where η is the packing fraction.

11.4 Discuss the perturbation theory and apply it to obtain expression for the free energy, internal energy and pressure.

11.5 What is the criteria for dividing the pair potential into the reference and perturbation part. How the perturbation theory is applied to a real fluid with the Lennard- Jones (12-6) potential.

11.6 Discuss the different choice of division of pair potential. Mention their merits and demerits.

11.7 Calculate the quantum correction to the free energy and pressure of the hard sphere fluid.

11.8 Show that the first order quantum correction to the thermodynamic properties can be obtained by replacing the actual diameter by an effective diameter.

11.9 Obtain the first order quantum correction to the thermodynamic properties of the Lennard- Jones (12-6) fluid.

11.10 Show that the first order quantum correction for an analytic potential is of the order of λ^2.

CHAPTER 12

STATISTICAL MECHANICS OF SOLIDS

12.1. Introduction

This chapter is concerned with the statistical mechanical theory of solids. A solid is characterised by its ability to retain its volume and shape. However a liquid retains its volume and has a shape dictated by that of the container. Solids have many features distinguishing them from liquids. The density of the liquid is only slightly less than that of the corresponding solid (with the exception of liquid water, whose density is slightly greater than that of solid ice). Like a solid, a liquid is only slightly compressible. Such similarities between a liquid and solid prompt us to consider them collectively as condensed matter.

Some substances exist, who retain their shape, but otherwise do not differ from liquids. These substances are called `amorphous', which include glass, plastics and various resins. Amorphous substances behave like liquids with an anomalously great viscosity owing to which at ordinary temperature they cannot flow. On rising the temperature, their viscosity diminishes, they gradually soften and acquire the ability of flow which is the usual properties of liquids.

Unlike this, when a solid is heated, it turns to liquid at the melting point. This is one of the important features distinguishing solids from amorphous ones.

For condensed matter the molecules are separated by only small distances (much less than a mean molecular diameter). At low temperature the mean interaction energy will be larger than the mean kinetic energy and the motion of the molecules will be controlled by the interaction forces. The atoms (or molecules) of solids are arranged in them not chaotically as in fluids but in a definite order characteristic of each substance. In a solid, such an ordered arrangement of atoms extends throughout the entire volume of a body (the so-called long-range order). Such substances with a regular arrangement of their particles are called crystalline solids.

12.2. Theory of Lattice Vibration

We consider the simple monatomic solids. A monatomic solid consists of a large number of atoms in a regular array, a lattice. Each atom has a position of equilibrium, its lattice point, about which it vibrates because of thermal agitation and zero-point energy.

In a solid, the vibration of atoms about their equilibrium positions is always small. Then, the Hamiltonian of a solid may be approximately a sum of terms, each representing a harmonic oscillator corresponding to a normal mode of lattice oscillation. Each normal mode is classically a wave of distortion of the lattiee planes – a sound wave. In quantum theory, these normal modes give rise to sound quanta- the so-called phonons.

Let us consider a solid crystal composed of N atoms, such that the position of the ith atom is specified by the coordinates r_i (with components $x_{i_1}, x_{i_2}, x_{i_3}$). Let the equilibrium position be defined by $\mathbf{R}_i$, (with components $X_{i_1}, X_{i_2}, X_{i_3}$), then the total potential energy can be expressed in the expansion form as

$$U(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_3) = U(R_1, R_2, \ldots, R_N) + \sum_{i=1}^{N} \sum_{\alpha=1}^{3} (\partial U/\partial x_{i\alpha})_{X_{i\alpha} = X_{i\alpha}} (x_{i\alpha} - X_{i\alpha})$$

$$+ (1/2) \sum_{i,j=1}^{N} \sum_{\alpha,\beta=1}^{3} (\partial^2 U/\partial x_{i\alpha}\, \partial x_{j\alpha})_{X_{i\alpha} = X_{i\alpha}} (x_{i\alpha} - X_{i\alpha})\,(x_{j\gamma} - X_{j\gamma}) + \ldots \quad (12.2.1)$$

In the equilibrium position, the potential energy is minimum and hence

$$(\partial U(X_{i\alpha})/\partial x_{i\alpha}) = 0$$

Thus, all the first derivatives vanish there. If $\xi_{i\alpha}=(x_{i\alpha}-X_{i\alpha})$ be the displacement of the atoms from their equilibrium position, then the kinetic energy of the system is given by

$$T = (1/2)m \sum_{i=1}^{N} \sum_{\alpha=1}^{3} \dot{x}_{i\alpha}^2 = (1/2)m \sum_{i} \sum_{\alpha} \dot{\xi}_{i\alpha}^2 \quad (12.2.2)$$

Thus, the Hamiltonian of the system has the form

$$H = \phi_0 + (1/2)m \sum_{i=1}^{N} \sum_{\alpha} \dot{\xi}_{i\alpha}^2 + \sum_{i,j} \sum_{\alpha,\gamma} \alpha_{ij}\, \xi_{i\alpha}\, \xi_{i\gamma} \quad (12.2.3)$$

where

$$\alpha_{ij} = (1/2)(\partial^2 U/\partial x_{i\alpha}\, \partial x_{i\gamma})_{X_{i\gamma} = X_{i\gamma}} \quad (12.2.4)$$

and ϕ_0 is the minimum energy. We choose it to be zero.

It is convenient to transform from the coordinates ξ_i to the normal coordinates q_i. Thus, there exists a transformation under which the potential energy does not contain any cross terms.

$$H = (1/2)m \sum_{i=1}^{3N} (\dot{q}_i^2 + \omega_i^2 q_i^2) \quad (12.2.5)$$

where $\omega_i (i = 1, 2, \ldots, 3N)$ are the characteristic frequencies of the normal modes of the system. Thus, in the normal form, the Hamiltonian of the system is expressed as the sum of 3N one-dimensional, non-interacting harmonic oscillators, whose characteristic frequencies ω_i are determined by the nature of the interatomic potential of the system.

According to classical theory, in case of simple harmonic motion, the average kinetic energy is equal to the average potential energy. Hence the average energy of vibration is twice its average kinetic energy. Thus, each vibrational mode, according to the law of equipartition of energy, has the energy kT, and the energy per atom will be 3kT, where k is the Boltzmann constant and T the absolute temperature.

Then the total energy of a solid containing N atoms is

$$U = 3NkT \quad (12.2.6)$$

so the specific heat at constant volume is

$$C_v = (\partial U/\partial T)_v = 3Nk \quad (12.2.7)$$

Thus the specific heat of a solid is constant. This is known as Dulong and Palit law.

However, experiments on the specific heat shows that it depends on temperature. The experimentally observed variation of the specific heat of Pb, Al and diamond with temperature is shown in Fig.12.1. At high temperature, it approaches to the value predicted by Dulong and Pelit law. However the specific heat decreases as the temperature is lowered till it approaches to zero at absolute zero.

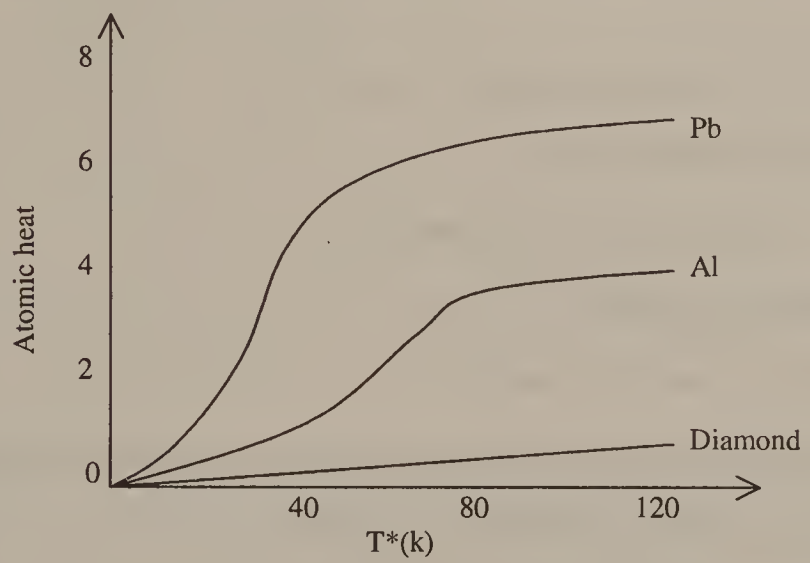


Fig.12.1. Atomic heat of Pb, Al and diamond as a function of temperature T.

The first explanation of the temperature dependence of specific heat was given by Einstein in 1907.

12.3. Einstein's Theory

Einstein proposed to employ quantum theory to derive the theory of specific heat of solids. According to him, each atom may vibrate in the field of neighbouring atoms with a certain frequency. It is assumed that the frequency is independent of direction and will be the same for all atoms.

The energy of atoms of a solid executing vibrations is assume to be discrete. According to quantum theory, the energy of an atom executing the simple harmonic motion for one degree of freedom is

$$E_n = (n + ½)\hbar\omega = \epsilon_0 + n\epsilon \qquad (12.3.1)$$

where ω is the frequency of a vibration and $\hbar = h/2\pi$ (h being the Plack's constant). Here $\epsilon_0 = \hbar\omega/2$ is the zero point energy of vibration and $\epsilon = \hbar\omega$.

The partition function for an atom with one mode of vibration is

$$Q_1 = \sum_n \exp[-(E_n/kT)] = \exp(\epsilon_0/kT)/(1 - \exp(-\epsilon/kT) \qquad (12.3.2)$$

Then the free energy is given by

$$A = \epsilon_0 + kT \ln [1 - \exp(-\epsilon/kT)] \qquad (12.3.3)$$

From this, other thermodynamic properties can be obtain. Thus the mean energy of an atom with one mode of vibration is

$$\langle E \rangle = \epsilon_0 + \epsilon (\exp(-\epsilon/kT)/(1 - \exp(-\epsilon/kT)) = \epsilon_0 + (\epsilon / (\exp(\epsilon/kT) - 1) \quad (12.3.4)$$

If the solid contains N atoms where N is the Avogadro number, the energy of one mole of the solid is

$$U = 3N\langle E \rangle = 3N\epsilon_0 + 3N\epsilon (1/(\exp(-\epsilon/kT) - 1)) \quad (12.3.5)$$

Then the specific heat at constant volume is given by

$$C_v = (\partial U/\partial T)_v = 3Nk (\epsilon/kT)^2 (\exp(\epsilon/kT)/(\exp(\epsilon/kT) - 1)^2) \quad (12.3.6)$$

Using the relation $\epsilon = \hbar\omega$, it can be rewritten as

$$C_V = 3NK(\hbar\omega/kT)^2 (\exp(\hbar\omega/kT)/(\exp(\hbar\omega/kT) - 1)^2) \quad (12.3.7)$$

This is the Einstein formula for the specific heat of solid. This equation shows that C_v depends on temperature.

Let us consider the specific heat in the limiting cases of temperature

(i) At low temperature, $\hbar\omega/kT \gg 1$ and (12.3.7) reduces to

$$C_V = 3NK(\hbar\omega/kT)^2 \exp(-\hbar\omega/kT)$$

giving

$$C_v \to 0, \text{ as } T \to 0.$$

(ii) At high temperature, where $\hbar\omega/kT \ll 1$, (10.3.7) can be expressed as

$$C_V = 3NK(1 + (\hbar\omega/kT) + \ldots) / (1 + (1/2)(\hbar\omega/kT) + \ldots)^2$$

From this, we find that

$$C_v \quad 3Nk, \text{ when } T \to \infty .$$

which is in agreement with Dulong and Petil law.

The variation of C_v with T is shown in Fig.12.2. The theoretical values are in agreement with the experimental data at low and high temperatures but it deviates at the intermediate temperatures.

Although the Einstein theory gives a general qualitative account of the observed behaviour of the specific heat of solid, there is no quantitative accordance between his theory and experiment. This quantitative discripancy is due to a serious draw back in this theory. It is assumed that the atoms in solids vibrate independently with the same frequency. But this is known to be wrong, since atom in a solid is under the field of interaction of other atoms. Taking the interaction of atoms in a solid into consideration Debye improved the theory of specific heat.

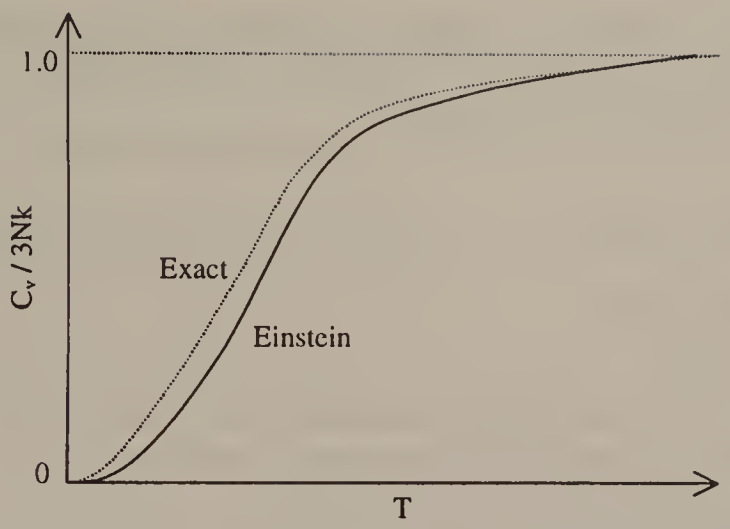


Fig.12.2. The specific heat $C_v/3Nk$ as a function of T according to the Einstein model. Experimental values are also shown.

12.4. Debye's Theory

According to Debye, atoms in a solid do not vibrate independently with the same frequency. When an atom moves in a certain direction from its equilibrium position, it acts with a certain forces on neighbouring atoms, which in turn displace from their equilibrium positions as a result of which the solid as a whole vibrates giving rise to an acoustic wave in the solid.

In quantum theory these modes of vibration give rise to quanta called "phonon". Thus the solid crystal can be regarded as a 'gas' of non-interacting phonons. A phonon is a spinless particle with definite momentum and energy. Since the spin of the phonons is zero, this gas obeys Bose-Einstein statistics. If a solid has N atoms, it has 3N normal modes. Each of the normal modes is characterised by its own frequency. Debye in 1912 assumed that these normal modes do not vibrate with a single frequency as Einstein assumed, but with a spectrum of frequencies, cut-off at a maximum frequency ω_D, called the Debye frequency, which is a characteristic of a crystal.

Let us assume that the solid is isotropic, so that the velocity of propagation of elastic waves is independent of their direction. A phonon of frequency ω has energy $\hbar\omega$ and momentum $\mathbf{P} = \hbar\mathbf{K}$, where $\mathbf{K}$ is the wave vector. For each wave vector $\mathbf{K}$, however, there is one longitudinal mode and two transverse modes. The longitudinal wave propagates with velocity u_l and transverse wave with velocity u_t. The frequency of these waves is linearly related to the magnitude of the wave vector $\mathbf{K}$ by $\omega = u_l|\mathbf{K}|$ or $\omega = u_t|\mathbf{K}|$.

The number of modes of vibrations in the volume V with the absolute magnitude of the wave vector ranging between K and K + dK is

$$(4\pi V/(2\pi)^3)K^2dK$$

Then the number of modes vibrations in the frequency range ω and $\omega+d\omega$ for the three directions of polarization (one longitudinal and two transverse modes) is given by

$$g(\omega)\,d\omega = (V/2\pi^2)\,((1/u_l^3) + (2/u_t^2))\,\omega^2 d\omega \qquad (12.4.1)$$

where in general, u_l and u_t are not equal.

The total number of modes of variation in a monatomic crystal is 3N. Therefore in Debye model, we must have

$$3N = \int_0^{\omega_D} g(\omega)\, d\omega = (V/6\pi^2)\,((1/u_l^3) + (2/u_l^2))\,\omega_D^3$$

or

$$\omega_D^3 = (18\pi^2 N/V)\,((1/u_l^3) + (2/u_l^2))^{-1} \qquad (12.4.2)$$

Using (12.4.2) we can rewrite (12.4.1) as

$$g(\omega)\, d\omega = (9N/\omega_D^3)\,\omega^2 d\omega \qquad (12.4.3)$$

According to quantum theory, the energy of the system using the Hamiltonian (12.2.5) is

$$E = \sum_{i=1}^{3N} (n_i + (1/2))\hbar\,\omega_i \qquad (12.4.4)$$

where $n_i = 0,1,2, \ldots$ are integers. The partition function for such a system consisting of all modes of vibration together is given by

$$Q_N = \sum_{(n_i)} \exp\left(-\sum_{i=1}^{3N} (n_i + (1/2))\hbar\omega_i/kT\right) = \sum_{(n_i)} \prod_{i=1}^{3N} \exp(-(n_i + (1/2)\hbar\omega_i/kT)$$

$$= \prod_{i=1}^{3N} [\exp(-\hbar\omega_i/kT)/(1 - \exp(-\hbar\omega_i/kT))\,] \qquad (12.4.5)$$

The last line of (12.4.5) is obtained by interchanging the summation with the product.

Then the free energy is given by

$$A = \sum_i [\,(1/2)\hbar\omega_i + kT \ln(1 - \exp(-\hbar\omega_i/kT))] \qquad (12.4.6)$$

Using (12.4.3), we can change the summation of (12.4.6) into integration. Then,

$$A = N\epsilon_0 + (9NkT/\omega_D^3) \int_0^{\omega_D} \ln(1 - \exp(-\hbar\omega_i/kT))\,\omega^2 d\omega \qquad (12.4.7)$$

where

$$\epsilon_0 = (9\hbar\omega_D/8)$$

is the zero-point energy. From this, other thermodynamic properties can be easily derived. Thus, the entropy is

$$S = (9\hbar/\omega_D^3 T) \int_0^{\omega_D} (\omega^3/(\exp(\hbar\omega/kT) - 1))\, d\omega - (9Nk/\omega_D^3) \int_0^{\omega_D} \ln(1 - \exp(-\hbar\omega_i/kT))\,\omega^2 d\omega \qquad (12.4.8)$$

and the internal energy is

$$U = N\epsilon_0 + (9N\hbar/\omega_D^3)\int_0^{\omega_D} (\omega^3/(\exp(\hbar\omega/kT) - 1))\, d\omega = N\epsilon_0 + 3NkT\, D(X_0) \qquad (12.4.9)$$

where $D(X_0)$ is the so-called Debye function

$$D(X_0) = (3/X_0^3)\int_0^{X_0} (X^3/(e^X - 1))\, dX \qquad (12.4.10)$$

with $X_0 = (\hbar\omega_D/kT) = (T_D/T)$

and $T_D = \hbar\omega_D/k$ is called the Debye temperature (see Table 12.1).

Table 12.1. Debye Temperature T_D(in K)

Crystals	T_D from specific heat	T_D from elastic constants
Al	398	402
Cu	315	329
Zn	308	305
Ag	225	216
Na	150	-
K	100	-
NaCl	308	320
KCl	230	246
C(Diamond)	~1850	-

Let us now calculate the Debye integral in both the limiting cases of temperatures:

(i) At high temperatures, $X \equiv \hbar\omega/kT \ll 1$ and (12.4.10) reduces to

$$D(X_0) = (3/X_0^3)\int_0^{X_0} X^3 [X + (X^2/2!) + (X^3/3!) + \dots]^{-1}\, dX$$

$$= (3/X_0^3)\int_0^{X_0} X^2 [1 - (1/2)X + (1/12)X^2 + \dots]\, dX$$

$$= 1 - (3/8)X_0 + (1/20)\, X_0^2 + \dots \qquad (12.4.11)$$

Hence, from (12.4.9) we get an expression for the energy of the solid as

$$U = 3NkT [1 + (1/20)\, (T_D/T)^2 + \dots] \qquad (12.4.12)$$

Thus, in the limit $T \to \infty$, we get

$$U = 3NkT$$

which is the well-known classical value for energy.

(ii) At low temperature, $X \gg 1$, in the first approximation we can replace the upper limit of integral of $D(X_0)$ by ∞. Thus

$$D(X_0) = (3/X_0^3) \int_0^{\infty} (X^3 / (e^X - 1)) \, dX = (3/X_0^3) \sum_{n=1}^{\infty} \int_0^{\infty} e^{-nX} X^3 \, dX = (\pi^4/5) (T/T_D)^3 \tag{12.4.13}$$

Substituting this value in (12.4.9) we obtain an expression for energy at low temperatures

$$U = N\epsilon_0 + (3\pi^4/5)NkT (T/T_D)^3 \tag{12.4.14}$$

in which the first term is zero-point energy. The T^4 law of the energy in the low temperature limit is the characteristic for a gas of massless bosons.

The specific heat of the solid at constant volume is given by

$$C_v = 3Nk [D(X_0) - X_0(dD(X_0)/dX_0] \tag{12.4.15}$$

giving

$$C_v = 3Nk [1 - (1/20) (T_D/T)^2 + \dots] \quad \text{at high temp} \tag{12.4.16a}$$

$$= (12\pi^4/5)Nk (T/T_D)^3 + \dots \quad \text{at low temp} \tag{12.4.16b}$$

Thus at low temperature

$$C_v \propto T^3$$

which is the Debye T^3 law. In the limit $T \to 0$, $C_v \to 0$. While when $T \to \infty$, $C_v \to 3Nk$, which is Dulong and Petit law.

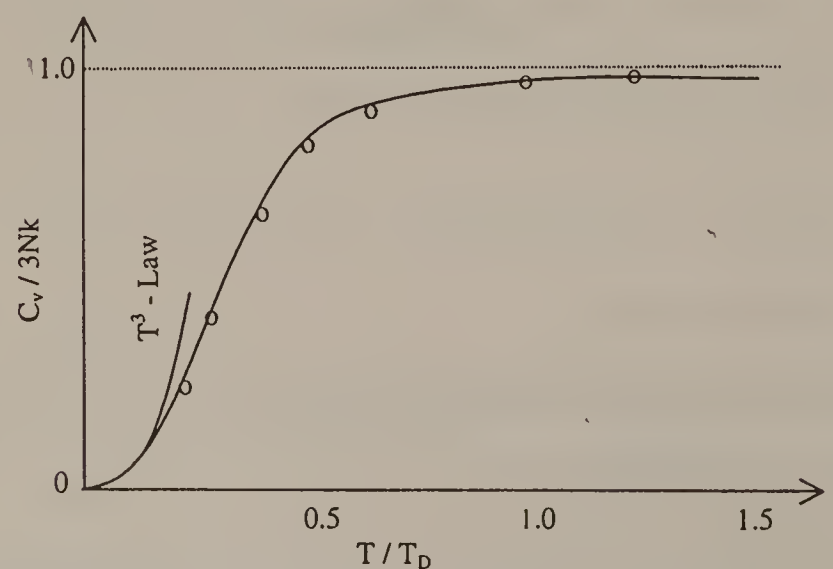


Fig.12.3. The specific heat $C_v/3$ Nk of solids as a function of temperature T/T_D according to the Debye theory. The circles represent the experimental values for copper

The variation of specific heat C_v with temperature (T/T_D) is shown in Fig.12.3. The agreement between theory and experiment is good throughout the range of temperatures. The T_3 law is also found to be in excellent agreement with the experimental observation at very low temperatures.

According to Debye's theory, the specific heat is some universal function of the ratio (T_D/T). In other words, according to the theory, the speciifc heats of solids are the same if the solids have the same values (T_D/T).

Because of its simplicity and general correctness, the Debye's model has found widespread applications in solid state physics. Debye's theory gives a good description of the variation of specific heat with temperature only for simple monatomic crystals. It is not applicable in practice to solids of more complex structure, since in such system the vibration spectrum is extremely complicated.

Despite the general success of the Debye's theory, it suffers from some defects. According to the Debye model, T_D is independent of temperature (see Table 12.1). In practice, T_D is found to vary with T. It is constant at the low and high temperature limits. Debye assumed that the sound velocity is constant for all wavelength. But recent study shows that the velocity depends on the wavelength.

These defects are basically due to the neglect of discrete atomic structure of solid.

12.5. Born's Theory

Debye's theory assumes the same maximum cut-off frequency ω_D for both the longitudinal and transverse modes. The maximum cut-off frequency ω_D depends on the elastic properties of the system. Generally this frequency may be different for direction of polarization. Born modified the Debye theory by introducing a different cut-off procedure. Born proposed to cut-off spectrum in such a manner that the longitudinal and transverse modes have the common minimum wavelength λ_{min}. This is theoretically more sound as it is in accordance with the theory of lattice vibration developed by Born and van Karman. Thus if we take the common minimum wavelength

$$\lambda_{min} = (4\pi V/3N)^{1/3}$$

we get two Debye frequencies.

$$\omega_D^l = (6\pi^2 N/V)^{1/3} u_l$$

$$\omega_D^t = (6\pi^2 N/V)^{1/3} u_t \qquad (12.5.1)$$

where ω_D^l and ω_D^t correspond to the longitudinal and transverse modes moving with the velocities u_l and u_t, respectively.

Treating the longitudinal and transverse modes separately, the total modes of vibration in a solid is given by

$$3N = \int g(\omega)d\omega = (V/2\pi^2)\left[(1/u_l^3)\int_0^{\omega_D^l} \omega^2 d\omega + (2/u_t^2)\int_0^{\omega_D^t} \omega^2 d\omega\right]$$

$$= (V/6\pi^2)\left[(\omega_D^3/u_l^3) + 2(\omega_D^t/u_t^3)\right] \qquad (12.5.2)$$

The frequency distribution of the cut off procedure adopted by Debye and Born are represented in Fig.10.4.(a,b).

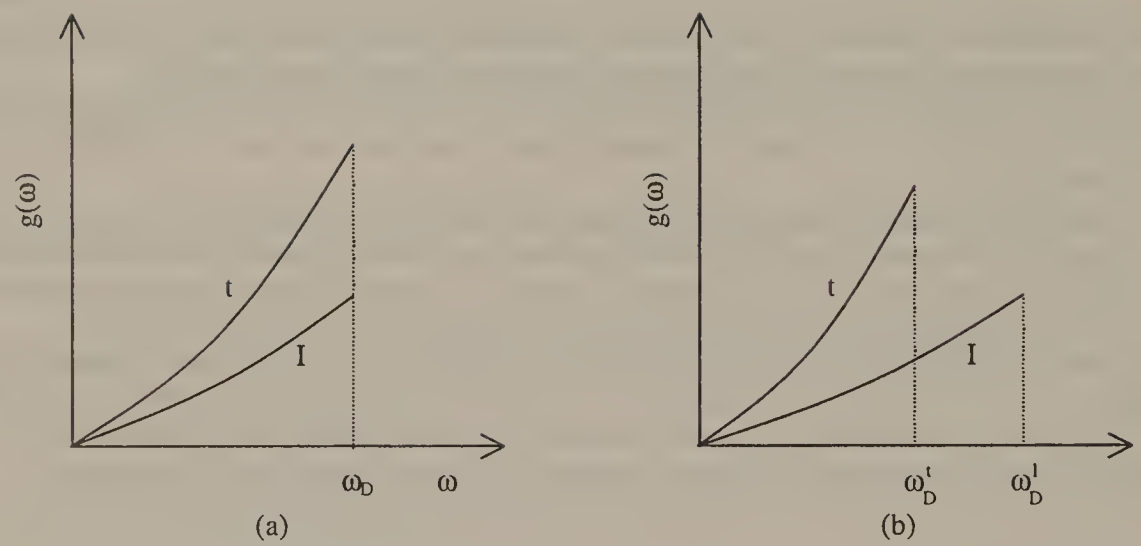


Fig.12.4(a) The Debye cut-off at the Debye frequency ω_D common to the longitudinal and transverse modes, and (b) The Born cut-off at ω_D^l and ω_D^t for the longitudinal and transverse modes.

Then (12.4.3) can be written as

$$g(\omega) = g_l(\omega) + 2g_t(\omega) \qquad (12.5.3)$$

where

$$g_l(\omega) = (3N/\omega_D^{l3})\omega^2$$

$$g_t(\omega) = (3N/\omega_D^{t3})\omega^2 \qquad (12.5.4)$$

Following the method discussed in Sec.(12.4), we obtain an expression for the total internal energy of the system.

$$U = N\epsilon_0 + NkT\,[D_l(X_l) + 2D_t(X_t)] \qquad (12.5.5)$$

where

$$\epsilon_0 = (3\hbar/8)\,(\omega_D^l + 2\omega_D^t) \qquad (12.5.6)$$

is the zero point energy and $D_l(X_l)$ and $D_t(X_t)$ are the Debye functions corresponding to the longitudinal and transverse modes, respectively.

Then Born's modification gives the following expression for the specific heat of solid at constant volume

$$C_v = Nk\,[F_l\,(T_D^l/T) + 2\,F_t(T_D^t/T)\,] \qquad (12.5.7)$$

where

$$F = D(X) - X(dD(X)/dX) \qquad (12.5.8)$$

Here T_D^l and T_D^t are the Debye temperature corresponding to the longitudinal and transverse modes.

$$T_D^l = \hbar\omega_D^l / k$$

$$T_D^t = \hbar\omega_D^t / k$$

From (12.5.7), we get

$$C_v = 3Nk\,[1 - (1/60)\,\{(T_D^l/T)^2 + 2\,(T_D^t/T)^2\} + \ldots] \quad \text{at high temp.} \qquad (12.5.9a)$$

$$= (4\pi/5)\,Nk\,[(T/T_D^l)^3 + 2\,(T/T_D^t)^3\,] \quad \text{at low temp.} \qquad (12.5.9b)$$

The Born model calculations have come into wide use, since the experimental data of sufficient accuracy are available for comparison.

This theory is suffering from the same defects as the Debye theory. This theory is not applicable to anisotropic crystals, where the velocity of elastic waves varies with direction. Further, the variation of velocity with wavelength is not taken into consideration.

12.6. Superconductivity in Metals

The phenomenon of superconductivity like superfluidity is a very fassinating subject. Many metals become superconductors below certain temperature – the temperature is different for different metals. When the temperature is reduced sufficiently, the metal conduct electricity without any resistance. This phenomenon was observed first by Kamerling Onnes in 1911. He found that the electrical resistance of a mercury sample disappeared below a critical temperature $T_c = 4.2$ K. It is this resistanceless motion (infinite conductivity), which gives name 'superconductivity' to this phenomenon. Many pure metal and metallic allows show 'superconductivity' at low temperature. At critical temperature T_c the system undergoes a phase transition from a normal state to a superconducting state.

We consider the normal electric conduction by a metal. The current is transmitted by the motion of 'free' electrons driven through the metal's crystal lattices by applied electric voltage. The electrons collide with atoms of the metal, this impedance of their motion constitutes the conductor's electrical resistance. The resistance decreases with decrease of temperature because the vibrating atoms in the lattice oscillate over smaller distance from their lattice positions and interfere with the electron's motion very weakly. It is reasonable to suppose that when the atom's vibrations are completely reduced to zero at absolute zero, resistance to flow of electrons might drop to zero. However it is found that resistance vanishes abruptly at several degree above absolute zero.

12.6.1 Fundamental properties of superconductors

In superconducting state, the metals and allows show the following remarkable properties:

(i) Infinite conductivity

When a metallic element or compound is cooled to a very low temperature, it abruptly loses electrical resistivity at a definite critical temperature T_c. It is an electronic transition in which the conduction electrons enter into an ordered state.

We assume the usual equations:

Ohm's law

$$\mathbf{I} = \sigma\mathbf{E}$$

and Maxwell equation

$$\partial \mathbf{B}/\partial t = -c \operatorname{curl} \mathbf{E}$$

These equation imply that the flux density **B** remains constant for any medium with infinite conductivity, because **E** vanishes inside the material.

(ii) **Meissner effect**

Let a normal metal be placed in a uniform magnetic field, the magnetic flux will pass through it (Fig.12.5b). When the sample is cooled and becomes superconducting, all the magnetic flux are expelled from the interior (Fig.12.5c). This is known as Meissner effect. In this case the constant value of **B** must always be taken to zero.

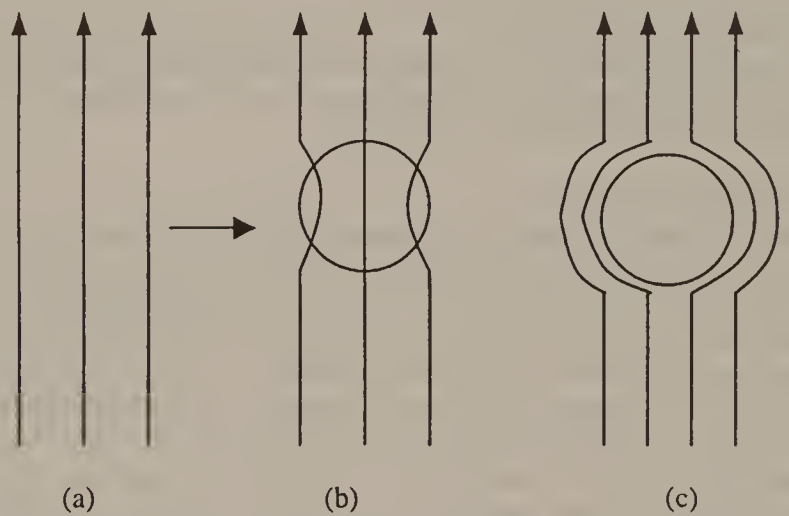


Fig.12.5. (a)Uniform magnetic field, (b) normal metal in magnetic field, and (c) superconductor in magnetic field.

It shows that a bulk superconductor behaves in an applied external field **H** as if inside the specimen **B** = 0. This means that inside the super conductor

$$\mathbf{B} = \mathbf{H} + 4\pi\mathbf{M} = 0$$

so that the magnetic susceptibility is

$$\chi = \mathbf{M}/\mathbf{H} = -1/4\pi$$

Thus the magnetic susceptibility is negative. Therefore, a superconductor is a 'perfect' diamagnet. This also shows that perfect diamagnetism and zero resistivity are two properties of the superconducting state.

The magnetization curve for a superconductor is shown in Fig.12.6. Pure specimens of many materials exhibit the behaviour of Fig.12.6a. They are called type I superconductors or soft superconductors. Other materials exhibit a magnetization curve of Fig.12.6b. They are known as type II superconductors.

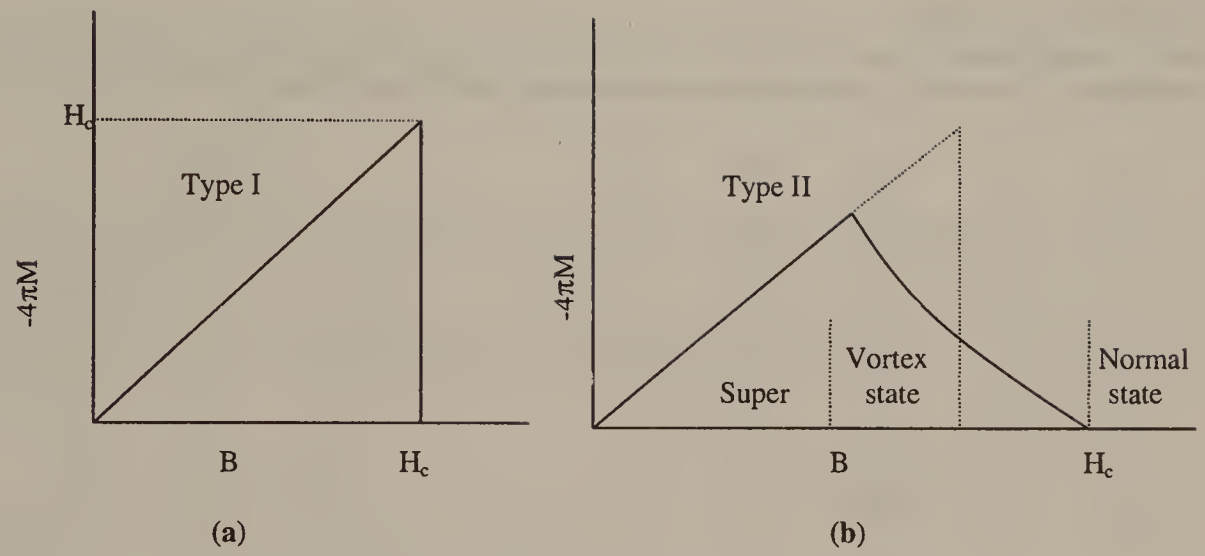


Fig.12.6. Magnetization curves for type I and type II superconductors.

(iii) **Critical field**

The Meissner effect occurs only for sufficiently low magnetic field. Let a pure superconductor be placed in a parallel magnetic field **H**, where there are no diamagnetic effect. If the sample is superconducting at a temperature T in zero field, there will be a critical field $H_C(T)$ above which the sample becomes normal and below $H_C(T)$ it is superconductor. Experimentally it is found that

$$H_C(T) = H_C(O)\,[1 - (T/T_C)^2]$$

The curve of $H_C(T)$ against T is roughly parabolic as shown in Fig.12.7.

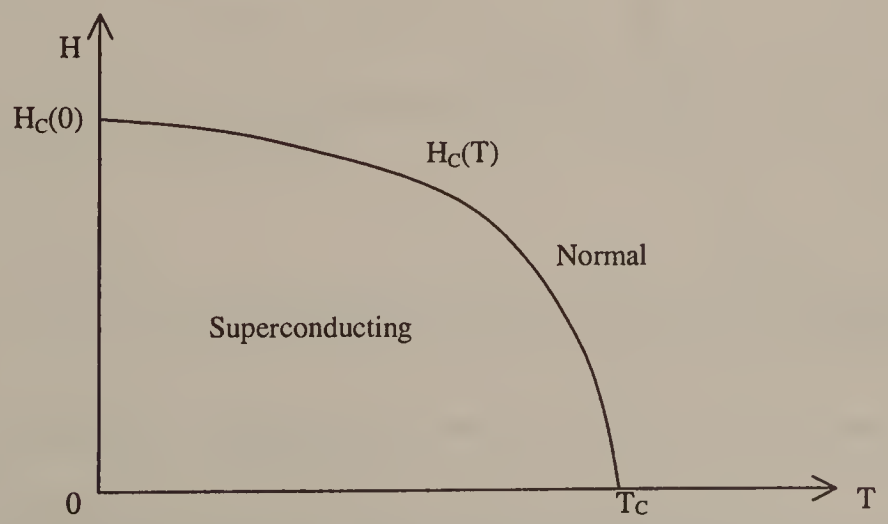


Fig.12.7. H_c-T curve for superconductor.

(iv) **Persistent currents**

Let a normal metallic ring be placed in a magnetic field perpendicular to its plane. When the temperature is lowered, the metal becomes superconducting and expels the magnetic flux.

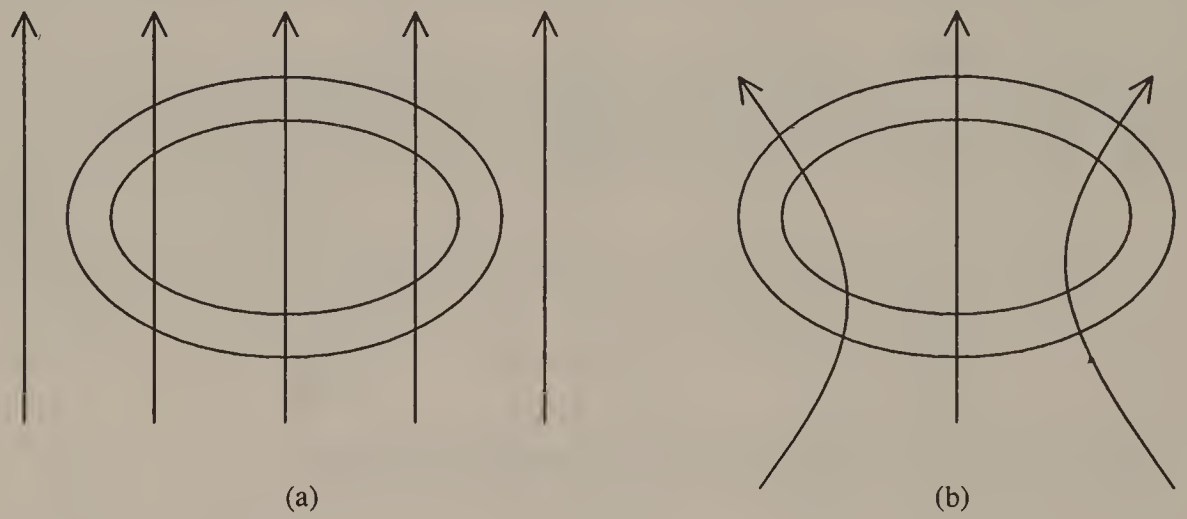


Fig.12.8. (a) Normal metal ring in a magnetic field and (b) superconducting ring in magnetic field

If the external field is then removed, no flux can pass through the superconducting metal and total trapped flux must remain constant, being maintained by circulating supercurrent in the ring itself. Such persistent currents have been observed.

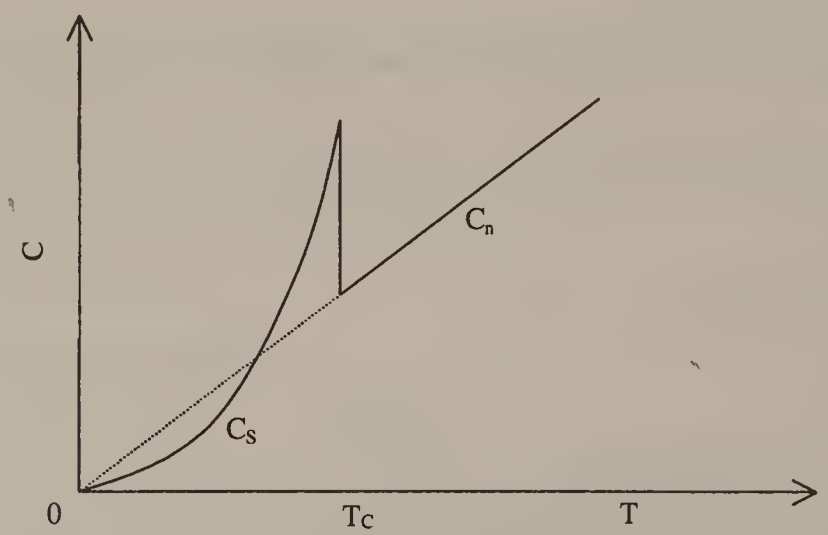


Fig.12.9. Variation of specific heat with temperature for superconductor

(v) **Specific heat**

A superconductor has distinct thermal properties. It has a discontinuous specific heat but no latent heat.

The electronic specific heat C_n in the normal metal varies linearly with temperature as

$$C_n = aT$$

In the superconducting states the specific heat is given by

$$C_S \propto \exp[-\Delta_0/kT]$$

It initially exceeds C_n for $T \leq T_C$, then drops below C_n and vanishes as $T \to 0$ (as shown in Fig.12.9).

(vi) **Isotope effect**
It is distinct property of superconductors. It is found that the ionic lattice plays an important role in superconductivity, for the transition temperature T_C varies with ionic mass M as

$$T_C \propto M^{-1/2}$$

This result indicates the importance of attractive electron-phonon interaction, which provides a mechanism for the formation of bound cooper pairs.

12.6.2. Thermodynamics of superconducting transition

The discovery of Meissner effect enabled Gorter and Casimir to give thermodynamic treatment of the superconducting phase transition. The thermodynamics of a superconducting transition in a magnetic field is perfectly analogous to that of the liquid vapour phase transition.

Let us start with the basic equations of electrodynamics. There are two fundamental fields **E** and **B**, defined by the Maxwell equations

$$\text{div } \mathbf{E} = 4\pi\rho \tag{12.6.1a}$$

$$\text{div } \mathbf{B} = 0 \tag{12.6.1b}$$

$$\text{curl } \mathbf{E} = -(1/c)(\partial \mathbf{B}/\partial t) \tag{12.6.1c}$$

$$\text{curl } \mathbf{B} = -(1/c)(\partial \mathbf{E}/\partial t) + (4\pi/c)\rho \mathbf{V} \tag{12.6.1d}$$

where **E** and **B** are electric and magnetic field, respectively, ρ is the total charge density moving with velocity **V** and c the velocity of light.

We can write

$$\rho = \rho_p + \rho_f$$

where $\rho_p = -\text{div } \mathbf{P}$ is the polarization density and ρ_f is a free charge density. With this help, (12.6.1a) becomes

$$\text{div}(\mathbf{E} + 4\pi\mathbf{P}) \equiv \text{div}\mathbf{D} = 4\pi\rho_f \tag{12.6.2}$$

where **P** and **D** are known as the polarization and displacement, respectively.

Similarly, the total current is separated into a magnetization current c curl **M**, a polarization current $\partial \mathbf{P}/\partial t$ and a free current $\mathbf{J}_f$ associated with the motion of free charges. Thus

$$\rho \mathbf{V} = c \text{ curl } \mathbf{M} + (\partial \mathbf{P}/\partial t) + \mathbf{J}_f \tag{12.6.3}$$

where **M** is the magnetization, then (12.6.1d) can be written as

$$\text{Curl } \mathbf{H} = (1/c)(\partial \mathbf{D}/\partial t) + (4\pi/c)\mathbf{J}_f \tag{12.6.4}$$

where

$$\mathbf{H} = \mathbf{B} - 4\pi\mathbf{M}$$

is the magnetic field. The first term of (12.6.4) is generally negligible in low frequency phenomena. Thus

$$\text{Curl } \mathbf{H} = (4\pi/c)\mathbf{J}_f \tag{12.6.5}$$

According to Poynting theorem, the energy flowing through a surface S in a short time dt is given by

$$W = -dt\,(c/4\pi) \int_S (\mathbf{E} \times \mathbf{H}).d\mathbf{S}$$

Applying the Gauss divergence theorem, the surface integral can be changed into the volume integral, giving

$$W = -dt\,(c/4\pi) \int_V \nabla.(\mathbf{E} \times \mathbf{H})dV \tag{12.6.6}$$

Using the vector relation

$$\nabla.(\mathbf{A} \times \mathbf{B}) = \mathbf{B}.(\nabla \times \mathbf{A}) - \mathbf{A}.(\nabla \times \mathbf{B})$$

we have

$$\nabla.(\mathbf{E} \times \mathbf{H}) = \mathbf{H}.(\nabla \times \mathbf{E}) - \mathbf{E}.(\nabla \times \mathbf{H}) \tag{12.6.7}$$

Substituting (12.6.1c) and (12.6.4) in (12.6.7), we get

$$\nabla.(\mathbf{E} \times \mathbf{H}) = -(1/c)\mathbf{H}.(\partial \mathbf{B}/\partial t) - (1/c)\mathbf{E}.(\partial \mathbf{D}/\partial t) - (4\pi/c)\mathbf{E}\,\mathbf{J}_f \tag{12.6.8}$$

Then (12.6.6) reduces to

$$W = (c/4\pi) \int_V [(1/c)\mathbf{H}.d\mathbf{B} + (1/c)\mathbf{E}.d\mathbf{D} + (4\pi/c)\mathbf{E}\,\mathbf{J}_f dt]\, dV$$

When the magnetic quantities are changed by small amount, the work done on the system is given by

$$W = (1/4\pi) \int_V (\mathbf{H}.d\mathbf{B})\, dV \tag{12.6.9}$$

and the work done per unit volume is

$$dw = (1/4\pi)\,\mathbf{H}.d\mathbf{B} \tag{12.6.10}$$

Then the change in Helmholtz free energy density is given by

$$df = -sdT + dw = (1/4\pi)\,\mathbf{H}.d\mathbf{B} - sdT \tag{12.6.11}$$

This shows that $f \equiv f(\mathbf{B},T)$. Then

$$df = (\partial f/\partial B)_T \cdot d\mathbf{B} + (\partial f/\partial T)_B \cdot dT$$

On comparison, we get

$$s = -(\partial f/\partial T)_B$$

$$\mathbf{H} = 4\pi(\partial f/\partial \mathbf{B})_T \tag{12.6.12}$$

where s is the entropy density and the volume is assumed to be constant.

According to the Meissner effect, a bulk superconductor in an external magnetic field **H** is characterised by the condition **B** = 0, independent of the way the state is reached. Thus, we infer that the superconductor is in true thermodynamic equilibrium. However it is not possible to manipulate the magnetic induction **B** directly, rather we control the magnetic field **H**. Thus we use the Gibbs free energy density defined as

$$g(T,H) = f - (1/4\pi)\,\mathbf{H}.\mathbf{B} \tag{12.6.13}$$

which gives

$$dg = df - (1/4\pi)\,\mathbf{H}.d\mathbf{B} - (1/4\pi)\,\mathbf{B}.d\mathbf{H} = -sdT - (1/4\pi)\,\mathbf{B}.d\mathbf{H} \tag{12.6.14}$$

with

$$s = -(\partial g/\partial T)_H \tag{12.6.15a}$$

$$B = -4\pi\,(\partial g/\partial H)_T \tag{12.6.15b}$$

Let us now consider a long super-conducting cylider in parallel magnetic field. If the magnetic field **H** is increased at constant temperature, (10.6.15b) gives

$$g(T, H) = g(T,0) - (1/4\pi)\int_0^H B(H')dH' \tag{12.6.16}$$

To a good approximation, the normal state of most superconducting elements is non- magnetic (i.e.**B** = **H**), then we get

$$g_n(T,H) = g_n(T,0) - (1/8\pi)H^2 \tag{12.6.17}$$

If **B** vanishes in superconductor, then from (12.6.16), we have

$$g_s(T,H) = g_s(T,0) \tag{12.6.18}$$

Two phases are in the thermodynamic equilibrium at the critical field H_c. Thus

$$g_s(T,H_c) = g_n(T,H_c) \tag{12.6.19}$$

This gives

$$g_s(T,0) = g_n(T,0) - (1/8\pi)H_c^2 \tag{12.6.20}$$

This equation shows that a negative condensation energy $(-H_c^2/8\pi)$ per unit volume accompanies the formation of the super conducting state. Further using (10.6.17) – (10.6.20), we obtain the general relation

$$g_s(T,H) - g_n(T,H) = (1/8\pi)[H^2 - H_c^2] \tag{12.6.21}$$

So that the superconducting phase is the equilibrium state for all $H < H_c(T)$.

Differentiating (12.6.21) with respect to temperature and using (12.6.15a), we get

$$s_s(T,H) - s_n(T,H) = (1/4\pi)H_c(T)\,(dH_c(T)/dT) \tag{12.6.22}$$

Experimentally $H_c(T)$ is given by

$$H_c(T) = H_c(O)\,[1 - (T/T_c)^2]$$

This shows that H_c decreases with increase of T so $dH_c/dT < 0$ and right hand side of (10.6.22) is negative, so that

$$s_s(T,H) < s_n(T,H)$$

At $T = T_c$, $H_c = 0$, so $s_s = s_n$. Thus the entropy of two phases are equal at critical temperature in the zero field. However at lower temperature the entropy of the superconducting phase is less than that of the normal ones. This shows that the superconducting state is the state of higher order.

The latent heat associated with the transition is

$$L = T(s_s - s_n)$$

which vanishes at $T = 0$ and at $T = T_c$.

Finally using the relation

$$c_H = T(\partial s/\partial T)_H$$

the difference in the electronic specific heat at constant field is given by

$$c_{SH} - c_{nH} = (T/4\pi)\,[(dH_c/dT)^2 + H_c(d^2H_c/dT^2)\,] \tag{12.6.23}$$

In particular, in absence of magnetic field i.e. at $T = T_c$, $H_c = 0$, the jump in the specific heat becomes

$$(c_{SH} - c_n)_{T_c} = (T_c/4\pi)\,[(\partial H_c/\partial T)_{T_c}]^2 \tag{12.6.24}$$

This relation is known as Rutger's formula. This is in agreement with the experimental observation and is in accordance with the fact that there is a discontinuity in the specific heat at T_c.

12.7. Ginzberg – Landau Theory of Superconductivity

The Ginzberg-Landau theory is the useful approach to handle the problem of superconductivity. The starting point of the theory is the free energy of the superconductor as a function of Ψ.

The phase transition at T_c indicates the presence of an ordered state in which the electrons are partially condensed into a frictionless superfluid. Ginzberg and Landau describe the condense state with a complex order parameter Ψ. The second order transition shows that Ψ vanishes for $T \geq T_c$ and increases in magnitude with increase of $T_c - T > 0$. The free energy density do not depend on the phase of the order parameter. Near T_c, the free energy density of the superconducting state in the zero field can be expanded in the form

$$f_{so} = f_{no} + a(T)\,|\Psi|^2 + (1/2)b(T)\,|\Psi|^4 + \ldots \qquad (12.7.1)$$

where f_{no} is the free energy density of the normal state in the zero field and a and b are real temperature dependent constants.

Ginzberg and Landau added a term

$$(1/2m^*)|-i\hbar\nabla\Psi|^2$$

in analogy with the Schrodinger equation, which tends to suppress spatial variation in Ψ. Here m^* is an effective mass

In the presence of magnetic fields, this term assumes the form

$$(1/2m^*)|(-i\hbar\nabla + e^*\mathbf{A}/c)\Psi|^2$$

where $-e^*$ is some integral multiple of the electron charge and

$$\nabla \times \mathbf{A} = \mathbf{B} \qquad (12.7.2)$$

which determines the magnetic field. Then the total free energy density of the superconducting state in a magnetic field is given by

$$f_s = f_{no} + a|\Psi|^2 + (1/2)b|\Psi|^4 + (1/2m^*)\,|(-i\hbar\nabla + e^*A/c)\Psi|^2 + (B^2/8\pi) \qquad (12.7.3)$$

where the last term is the energy density of the magnetic field. Here $|\Psi|^2 = \Psi^*\Psi$. We choose Ψ such that

$$|\Psi|^2 = (1/2)\,n_s^*$$

where n_s^* is the effective superelectron density. Experimentally it found

$$e^* = 2e$$

$$m^* = 2m$$

$$n^* = (1/2)n_s \qquad (12.7.4)$$

Integrating (12.7.3) over the total volume V, the free energy of the sample is

$$F_s = F_{no} + \int_V \{(B^2/8\pi) + (1/4m)\,|(-i\hbar\nabla + (2e/c)\mathbf{A})\Psi|^2 + a|\Psi|^2 + (1/2)b\,|\Psi|^4\}\,dV \qquad (12.7.5)$$

where $F_{no} = \int_V f_{no}\, dV$ is the free energy of the sample in the normal state in absence of the magnetic field. The condition of thermodynamic stability requires that (12.7.5) be stationary with respect to Ψ and A. Varying the integral with respect to Ψ^*, we find

$$\delta F_s = \int_V \{(1/4m)\,(-i\hbar\nabla + (2e/c)\mathbf{A})^2\,\Psi + a\Psi + b|\Psi|^2\Psi\}\,\delta\Psi^* dV \qquad (12.7.6)$$

Putting $\delta F_s = 0$, the integrant of volume integral is zero. For arbitrary $\delta\Psi^*$, we obtain

$$(1/4m)\,(-i\hbar\nabla + (2e/c)\mathbf{A})^2\,\Psi + a\Psi + b|\Psi|^2\Psi = 0 \qquad (12.7.7)$$

Similarly, varying the integral of (12.7.5) with respect to **A**, we get

$$(c/4\pi)\,\nabla \times \mathbf{B} = (ie\hbar/2m)\,(\Psi^*\nabla\Psi - \Psi\nabla\Psi^*) - (2e^2/mc)|\Psi|^2\mathbf{A} \qquad (12.7.8)$$

Using the Maxwell equation

$$\nabla \times \mathbf{B} = (4\pi/c)\,\mathbf{J} \qquad (12.7.9)$$

$$\mathbf{J} = (ie\hbar/2m)\,(\Psi^*\nabla\Psi - \Psi\nabla\Psi^*) - (2e^2/mc)|\Psi|^2\mathbf{A} \qquad (12.7.10)$$

Equations (12.7.7), (12.7.9) and (12.7.10) form complete set of Ginzberg-Landau equations.

In the absence of magnetic field (**A** = 0), (12.7.7) takes the form

$$(\hbar^2/4m)\,\nabla^2\Psi + a\Psi + b|\Psi|^2\Psi = 0 \qquad (12.7.11)$$

which has solutions

$$\Psi = 0$$

or

$$|\Psi|^2 = -a/b \qquad (12.7.12)$$

The first solution clearly represents the normal state, i.e

$$f_{so} = f_{no}$$

The second solution is physically acceptable and represents the superconducting state with the corresponding free energy density

$$f_{so} = f_{no} - (1/2)\,(a^2/2b) \qquad (12.7.13)$$

For $T < T_c$, Ginzberg and Landau assumed

$$|\Psi|^2 = -a/b = \alpha\,(T_c - T) \qquad (12.7.14)$$

Then (12.7.13) can be expressed as

$$f_{so} = f_{no} - (\alpha^2/2b)\,(T_c - T)^2\,, \qquad T < T_c \tag{12.7.15}$$

and the specific heat is

$$C_{so} - C_{no} = (\alpha^2/b)\,T_c \qquad T < T_c \tag{12.7.16}$$

which has a discontinuity at the transition point.

This choice predicts that

$$n_s(T) \propto (T_c - T)$$

Thus the superconduting electron density decreases linearly to zero at the transition point.

In a weak magnetic field, we can neglect the influence of the field on $|\Psi|^2$ by (12.7.14). Then (12.7.10) reduces to

$$\mathbf{J} = -(2e^2/mc)|\Psi|^2\,\mathbf{A} = -\Lambda_s\,\mathbf{A} \tag{12.7.17}$$

where $\Lambda_s = e^2 n_s/mc$ is a constant. Taking the curl of both sides of (12.7.17), we get

$$\nabla \times \mathbf{J} = -\Lambda_s\,\nabla \times \mathbf{A} = -\Lambda_s\,\mathbf{B}$$

where $\mathbf{B} = \nabla \times \mathbf{A}$. Using (12.7.9), we obtain

$$\nabla \times \nabla \times \mathbf{B} = -(4\pi\Lambda_s/c)\mathbf{B}$$

$$\nabla \times \nabla \times \mathbf{J} = -\Lambda_s\,\nabla \times \mathbf{B} = -(4\pi\Lambda_s/c)\mathbf{J}$$

With the help of relation

$$\nabla \times \nabla \times \mathbf{A} = \nabla(\nabla.\mathbf{A}) - \nabla^2\mathbf{A}$$

We find

$$\nabla^2\mathbf{B} = (4\pi\Lambda_s/c)\mathbf{B}$$

$$\nabla^2\mathbf{J} = (4\pi\Lambda_s/c)\mathbf{J} \tag{12.7.18}$$

(12.7.18) is the London equation, with the penetration depth

$$\delta(T) = (c/4\pi\Lambda_s)^{1/2} = (mc^2/4\pi e^2 n_s)^{1/2} = (mc^2 b/8\pi e^2\alpha(T_c - T))^{1/2} \tag{12.7.19}$$

The Ginzberg-Landau equations contain another characteristic length

$$\xi(T) = \hbar/(4m|a|)^{1/2} = h/(4m\alpha(T_c - T))^{1/2} \tag{12.7.20}$$

This length is known as the Ginzberg-Landau coherence length. It becomes large when $T \to T_c$.

We can write the solution of (12.7.18) as

$$\mathbf{B} = \mathbf{B}_0 \exp(-r/\delta)$$

$$\mathbf{J} = \mathbf{J}_0 \exp(-r/\delta) \qquad (12.7.21)$$

where r is the distance inside the metal from the surface. These equations suggest that **B** and **J** disappear exponentially inside the metal surface and are almost zero for large value of r. This explains the Meissner effect.

It is important to emphasize that the characteristic length $\delta(T)$ and $\xi(T)$ are both phenomenological quantities defined in terms of a and b. It is convenient to introduce the Ginzberg-Landau parameter defined as

$$K = \delta(T)/\xi(T) = (mc/\hbar c)(b/2\pi)^{1/2} \qquad (12.7.22)$$

which is independent of temperature near T_c.

The material for which $\xi \gg \delta$ are called type I superconductors. A type I superconductor will expel all currents and external magnetic field **H** except for a thin layer of thickness δ near the surface. If $K = \delta/\xi > 2^{1/2}$, the Ginzberg-Landau equations can have vortex solution in analogy with superfluids. Such a superconductor is called a type II superconductor.

12.8. BCS Theory

In this section, we discuss a brief outline of the theory of superconductivity developed by Bardeen, Cooper and Schrieffer- usually known as BCS theory.

The electrons interact with the vibrations of the atoms in the lattice. Due to these interactions, there is a small net effective interaction between the electrons. The result is that the electrons form together bound pairs.

Now we know that a single electron (having spin i = ½) is a Fermi particle obeying Fermi-Dirac statistics. A bound pair of electrons have the resultant spin either 0 or 1, so a bound pair will act as a Bose particle, which obeys Bose-Einstein statistics. Thus these bound pairs have properties which are similar to those of bosons and at sufficiently low temperature, condense into the superconducting state.

The energy of pairing is very weak. Only a small temperature is needed to through the electrons apart by thermal agitation and convert them back to 'normal' electrons. But when we reduce the temperature sufficiently low so that they react at the absolutely lowest state, then they do collect in pairs. The two electrons, which form the pair, are really spread over a considerable distance and the mean distance between the pairs is relatively smaller than the size of a single pair. Thus electrons in a metal form pairs. This fundamental point in the theory of superconductivity was first explained in the BCS theory. For a more detailed treatment the reader may consult the original papers (Bardeen et al, 1957) or the monograph of Schrieffer (1964).

12.9. High Temperature Superconductor

The superconductivity at high temperature is very interesting subject at present. We have found that superconductor is the state of matter in which the electrical resistance of the material goes to zero suddenly below T_c. The highest value of T_c was about 23 K in Nb_3Ge till 1986. Research workers are engaged in raising T_c. Bednorz and Muller realized a few year ago that oxide system with strong electron-phonon interactions with lattice deformations might be prone at high T_c superconductivity. They showed in 1986 that the superconducting state was attend at about 30 K. This was a turning point in the history of superconductivity research. After this work, there has been tremendous increase in the activity on these oxide to push up T_c as high as possible.

Many workers have succeeded in obtaining $T_c \sim 90$ K. So far the practical application is concerned, the progress is not so well. This is due to the fact that these materials are very brittle and there are considerable difficulties in drawing them into wires.

Problems

12.1 Derive Einstein's theory for the specific heat of solid. Discuss its limitations. How it has been modified by Debye.

12.2 Distinguish between assumptions of Einstein's and Debye's theories of specific heat of solids. Show that when these theories reduce to Dulog and Petit law.

12.3 The energy for one mode of vibration with frequency ω is $(n+1/2)\hbar\omega$. Show that the mean energy per mode of vibration is
$\epsilon = (\hbar\omega/2) + (\hbar\omega/(\exp(\hbar\omega/kT) - 1))$

12.4 If the energy for one mode of vibration with frequency ω is $n\hbar\omega$, where n is integer, then show that the mean energy per mode of vibration is given by
$\langle\epsilon\rangle = \hbar\omega/(\exp(\hbar\omega/kT) - 1)$
Explain why $\langle\epsilon\rangle = kT$ is not valid at low temperature.

12.5 Obtain the mean energy of a harmonic oscillator on the basis of quantum statistics. Hence discuss the Debye formula for the specific heat of a solid at low temperature.

12.6 Deduce the partition function for a Debye model of solid. Show that at low temperature, the specific heat of such a solid varies T^3.

12.7 Derive the Debye formula for the specific heat of one-dimensional solid at low temperature.

12.8 Derive the Debye formula for the specific heat of two-dimensional solid.

12.9 Show that the specific heat at low temperature for n-dimensional solid body obeys the law $C_v \sim T^n$.

12.10 Discuss Debye's theory for specific heat of solid. Explain, how it has been modified by Born.

12.11 Show that at low temperature, the specific heat of a solid can be expressed in the form
$C_v = aT + bT^3$.
Discuss how far it agrees with the experimental results.

12.12 What is superconductor ? Discuss its fundamental properties.

12.13 Discuss the thermodynamic properties of superconductivity transition.

12.14 Derive Ginzberg-Landau equations.

12.15 Using Ginzberg-Landau equations, obtain Landon equation and solve it.

12.16 Derive Ginzberg-Landau parameter. Show that it is independent of temperature near T_c.

CHAPTER 13

PHASE TRANSITION AND CRITICAL PHENOMENA

13.1. Phase Transitions

One of the most interesting problems in equilibrium statistical mechanics is the problem of phase transitions. Matter usually exists in the solid, liquid and gas phases. Solids are rigid and give sharp Bragg reflection in a diffraction experiment, demonstrating an ordered arrangement of atoms or molecules. Liquid and gas are fluid. There is no long-range order in the distribution of atoms or molecules in the fluid. Phase transitions are the transition of a matter from one phase to another which co-exists with the first. Such transitions involve a change in the mutual arrangement of molecules and in the thermodynamic properties of the system. Phase-transition points are classified as follows: the solid-liquid phase-transition point is called the melting point, the liquid-vapour phase-transition point is known as the boiling point and the solid-vapour phase-transition point is referred to as the sublimation point. We are all familiar with boiling water and the transition of a gas to liquid under compression, which are simple examples of phase transitions.

To specify the phase transition boundry, it is important to refer to a diagram of state which describes the relatioship between pressure, volume and temperature. A diagram of this kind for a one-component system is given in Fig.13.1 being a P-V diagram. The three phases may be in equilibrium only at a definite temperature and pressure, specific to a given system. The liquid and gaseous states

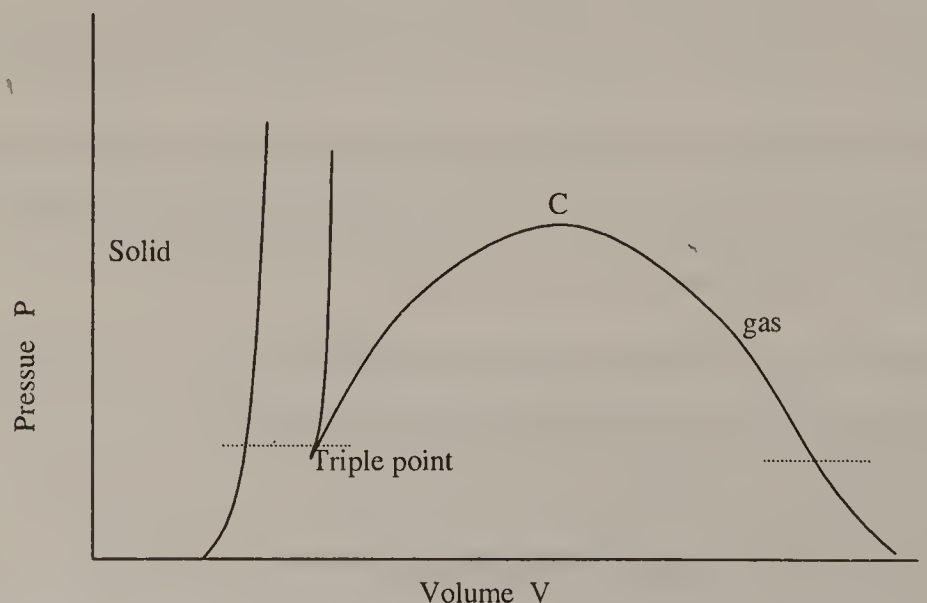


Fig.13.1. P-V phase diagram of one-component system in which triple and critical points are marked.

are separate only over a certain region of PVT space. At high temperatures and pressure these two states become one. Figure 13.1, which shows pressure as a function of volume, has the critical point C as the apex of the co-existence curve.

Phase transitions may be of the first and the second order. The first order transition is accompanied by a discontinuous change of internal energy and specific volume. In the process of phase transition of the first order, heat is evolved or absorbed. The solid-liquid and liquid-gas transitions are of the first order.

Phase transition of the second order is a transition in which the internal energy and specific volume change smoothly, and no heat is evolved or absorbed. Examples of such transitions are the transition of iron to the paramagnetic state at the Curie point and that of liquid He I to liquid He II at T_λ temperature.

13.2. Conditions for Phase Equilibrium

We consider a system consisting of two phases 1 and 2, which can exist simultaneously in equilibrium with one another.

As discussed in Sec.1.7, the conditions for the phase equilibrium are

$$T_1 = T_2 \text{ (thermal equilibrium)} \tag{13.2.1a}$$

$$P_1 = P_2 \text{ (mechanical equilibrium)} \tag{13.2.1b}$$

$$\mu_1 = \mu_2 \text{ (chemical equilibrium)} \tag{13.2.1c}$$

Thus, if two phases are in equilibrium; the temperatures, pressures and chemical potentials of these phases must be equal. If the chemical potentials are expressed as functions of pressure and temperature, then

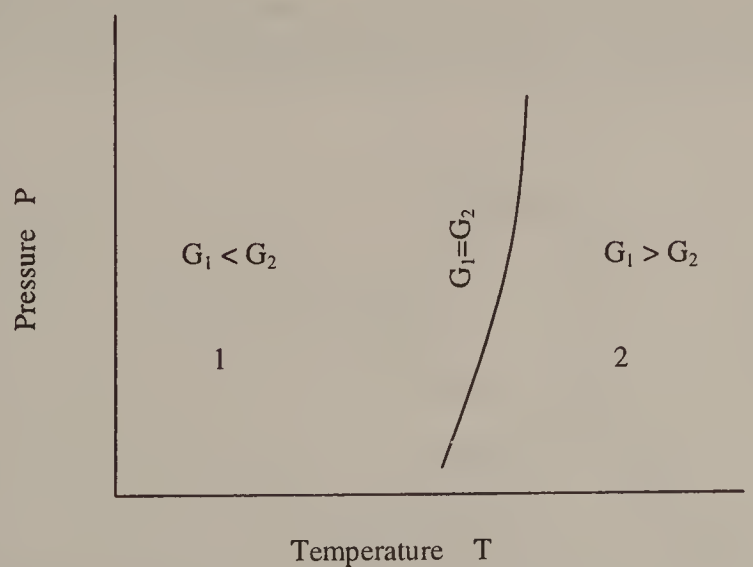


Fig.13.2. The phase equilibrium curve (G_1-G_2) separating two phases 1 and 2, respectively

$$\mu_1(P, T) = \mu_2(P, T) \tag{13.2.2}$$

where P and T are the common pressure and temperature of the two phases in equilibrium.

Equivalently, the molar Gibb's free energies of the two phases are equal, i.e.

$$G_1(P, T) = G_2(P, T) \tag{13.2.3}$$

which defines a curve in the (P, T) plane as shown in Fig.13.2. At a point on the curve, the Gibb's free energies of two phases are same. Two phases cannot be in equilibrium with each other at all pressures and temperatures.

13.3. First-order Phase Transition: The Clausius Clayperon Equation

The thermodynamic state of a homogeneous one-component system is determined by two thermodynamic variables, for example, the pressure P and temperature T. Let us consider two phases 1 and 2 in equilbrium. It is known that the phase equilbriums satisfy the condition

$$G_1(P, T) = G_2(P, T) \tag{13.3.1a}$$

or

$$g(P, T) = G_1(P, T) - G_2(P, T) = 0 \tag{13.3.1b}$$

Equation (13.3.1) can be solved to give the phase equilibrium curve of P as a function of T – (i) the melting curve in the case of the solid-liquid transition, or (ii) pressure curve in the case of the liquid-gas transition. It is also possible that the equilibrium of three phases is governed by the condition

$$G_1(P, T) = G_2(P, T)$$

$$G_2(P, T) = G_3(P, T) \tag{13.3.2}$$

These equations have solutions for specific pair of values (P_{tr}, T_{tr}) called triple points. One component systems have a single triple point, where three phases are simultaneously present in equilibrium. This is illustrated in Fig.13.3, where regions 1, 2 and 3 are three phases of the same system. It is noted that the equilibrium of more than three phases of the same system is impossible.

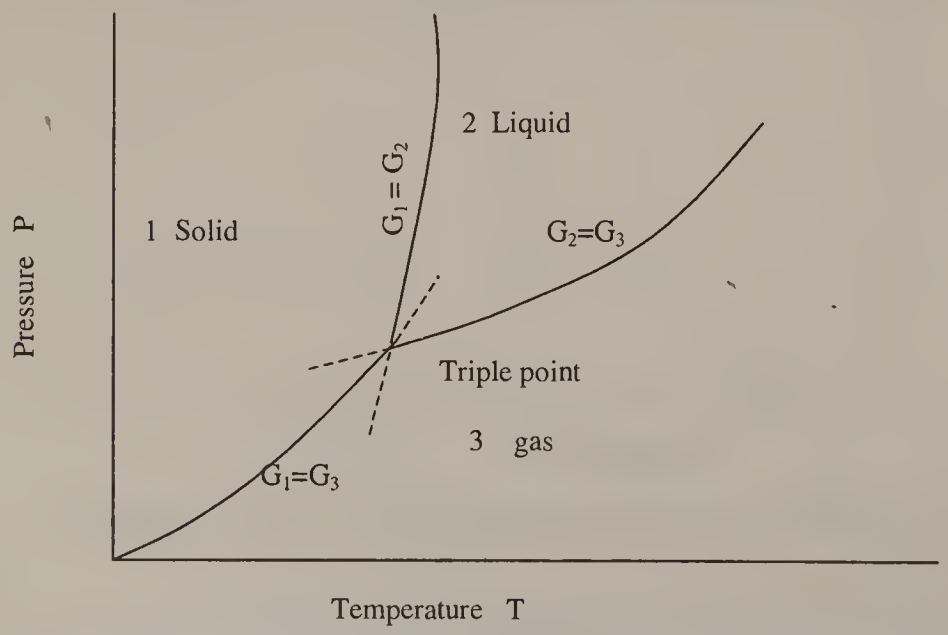


Fig.13.3. Phase diagram of one-component system possessing one triple point

Let the molar Gibb's free energies of the two phases be plotted in Fig.13.4 as functions of temperature T at constant pressure. The curves intersect at the temperature T_o at which the two phases can exist in equilibrium. At temperatures below T_o, the first phase is stable and above T_0, the second phase is stable. This is due to the fact that the stable state is one where G is smaller. Since entropy is a positive quantity, G must be a decreasing of T. If the phase 1 is stable for $T < T_0$, then at the point of interaction of two phases,

$$(\partial G_1/\partial T)_P > (\partial G_2/\partial T)_P \qquad (13.3.3)$$

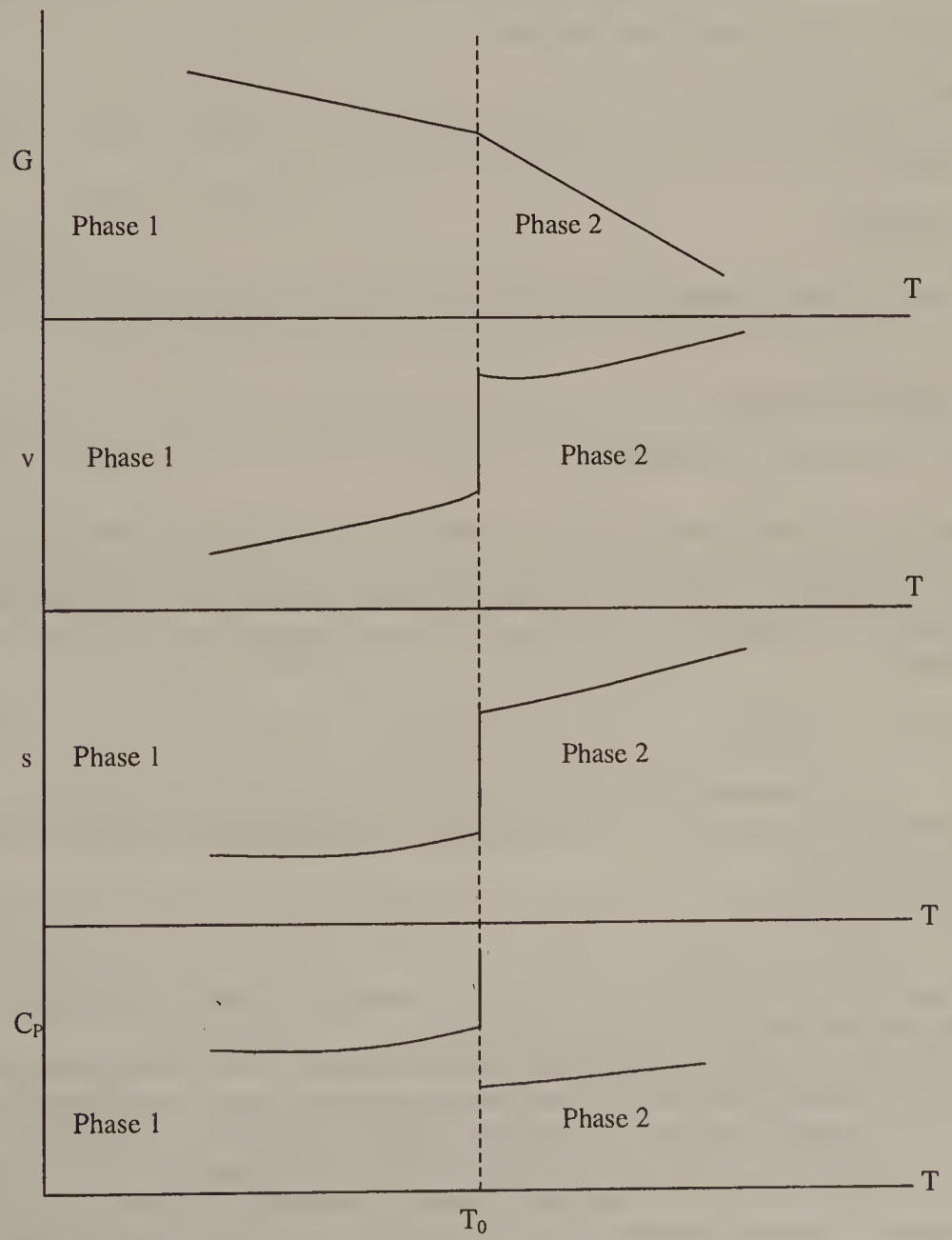


Fig.13.4. The variation of G, v, s and C_p during the first order transition

Let us change the temperature of each of the phases by dT and the pressure by dP in such a way that the two phases continue to be in equilibrium in the new states. Then in the new condition, the Gibb's free energies of the two phases will obviously be equal, i.e.

$$g(P + dP, T + dT) = 0 \tag{13.3.4}$$

We make a Taylor series expansion of g

$$g(P+dP, T+dT) = g(P,T) + (\partial g/\partial P)_T\, dP + (\partial g/\partial T)_P\, dT = 0 \tag{13.3.5}$$

The function g is always zero at equilibrium, and we get

$$(\partial g/\partial P)_T\, dP + (\partial g/\partial T)_P\, dT = 0 \tag{13.3.6}$$

Since,

$$v = (\partial G/\partial P)_T$$

$$s = -(\partial G/\partial T)_P \tag{13.3.7}$$

where v and s are the molar volume and molar entropy, respectively. Equation (13.3.6) gives the equation of the phase transition boundary as

$$(s_2 - s_1)dT = (v_2 - v_1)dP$$

or

$$dP/dT = (s_2 - s_1)/(v_2 - v_1) = \Delta s/\Delta v \tag{13.3.8}$$

where s_1, v_1 and s_2, v_2 are the molar entropies and volumes of the two phases. Equation (13.3.8) is known as the Clausius-Clapeyron equation. The phase transition is accompanied by the evolution or absorption of a certain quantity of heat, known as the latent heat of transition or simply the heat of transition. We know that the pressure P and temperature T remain constant during the transition of phase; so we obtain

$$T(s_2 - s_1) = H_2 - H_1 = L \tag{13.3.9}$$

where $L = T(s_2 - s_1)$ is the latent heat per unit mass of the transition and the quantity $(H_2 - H_1)$ is the difference between the enthalpies of the coexisting phases. Substituting this value, the Clausius-Clapeyron equation becomes

$$dP/dT = L/T(v_2 - v_1) = L/T\Delta v \tag{13.3.10}$$

Thus the latent heat L and volume change Δv, in a first order transition, are related to the slope of the phase equilibrium curve by the Clausius-Clapeyron equation.

During the first order transition, the Gibb's function is continuous but the first order derivatives of the Gibb's function change discontinuously. These derivatives are the volume $v = (\partial g/\partial P)_T$, which changes from v_1 to v_2 and the entropy $s = -(\partial G/\partial T)_P$ which changes from s_1 to s_2. These are demonstrated in Fig.13.4. There is a 'jump' in both specific volume v and entropy s.

We can also explain the behaviour of other thermodynamic properties, for example, specific heat C_P during the first order transition. We know that during transition both P and T are constant. Thus, when P is constant, dT = 0 and when T is constant dP = 0. Thus the specific heat C_P is

$$C_P = T(\partial s/\partial T)_P = \infty \qquad (13.3.11)$$

The variation of C_P is also shown in Fig.13.4. It remains finite up to the transition temperatures in the phase 1, and becoming infinity at the transition temperature and then returning to a finite value for phase 2.

From (13.3.3), it is clear that $s_2 > s_1$ and hence, the latest heat is always positive. Equation (13.3.10) may be used to explain melting, vaporization and sublimation.

For the liquid-vapour phase transition, the volume change $\Delta v = v_g - v_l$ is always positive and hence, dP/dT is greater than zero, i.e. the boiling point increases with increase in pressure. If the vapour pressure is low, $v_g \gg v_l$ and in this case (13.3.10) takes the form

$$dP/dT = L_v/Tv_g$$

where L_v is the latent heat of vaporization. Regarding the vapour as an ideal gas, $v_g = RT/P$, and hence

$$dP/P = (L_v/R)\,(dT/T^2) \qquad (13.3.12)$$

On integration we get

$$P(T)/P_c(T_c) = \exp\,[(L_v/R)((1/T_c) - (1/T))\,] \qquad (13.3.13)$$

where P_c and T_c are the critical pressure and critical temperature respectively, corresponding to the critical point C (Fig.13.1). In deriving (13.3.13), we have assumed that L_v is constant. However, the heat of vaporization L_v depends on temperature. Using the simplest linear dependence

$$L_v = a - bT$$

where a and b are constants, (13.3.12) gives

$$\ln(P(T)/P_c(T_c)) = (a/R)((1/T_c) - (1/T)) + (b/R)\ln(T_c/T) \qquad (13.3.14)$$

which is a relation between pressure and temperature.

In case of the solid-liquid phase transition, (13.3.10) can be presented as

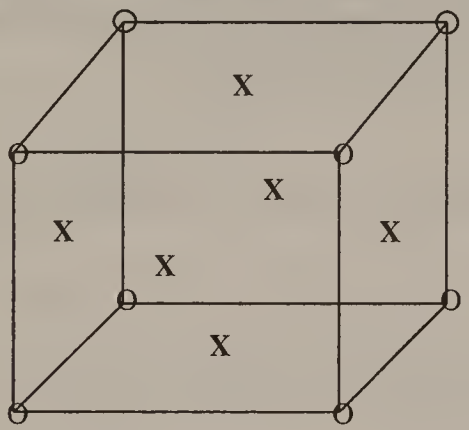
$$dP/dT = L_m / T(v_l - v_s) \qquad (13.13.15)$$

where L_m is the latent heat of melting. In this case v_l and v_s are usually close to each other, and two cases are possible: (i) the volume change $\Delta v = v_l - v_s$ is positive, then $dT/dP > 0$, i.e. the melting point increases with increase in pressure, and (ii) the volume Δv is negative, then $dT/dP < 0$ i.e. the melting point decreases with increase in pressure.

Near the triple point, L and Δv are generally much larger for the liquid-gas transition than for melting. The molar volume of a gas is usually much larger than that of a liquid or solid under these conditions, so that we can neglect the volume of the liquid in comparison with that of gas. Thus, the volume change on vapourisation is practically equal to the volume of the gas. On the other hand the volume change on the melting is very small. The latent heat of vapourisation of argon is approximately 6000 J mol^{-1} while the latent heat of melting of argon is roughly 1200 J mol^{-1}. On the liquid-gas transition of argon, the change in entropy $\Delta S/Nk$ 10. On the other hand, on the solid-liquid transition of argon, the change in entropy $\Delta S/Nk$ 2.

13.4. Second-Order Phase Transition

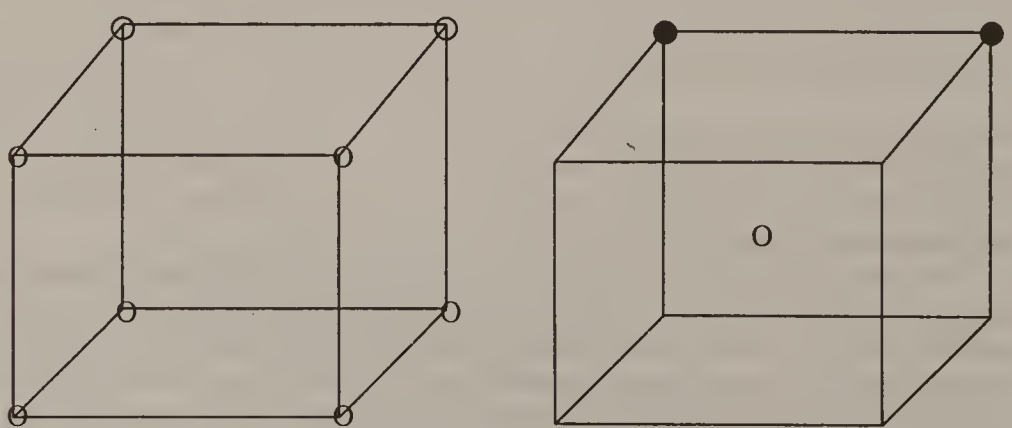
A phase transition of the second order is continuous in the sense that the state of the system changes continuously. But the symmetry changes discontinuously at the transition point. The transition of phases of different symmetry (such as different crystal modifications) cannot take place in a continuous manner as is possible between liquids and gases. In the case of the transition between different crystal modifications, there is a sudden rearrangement of the crystal lattice, and the state of the system changes discontinuously. In such a transition, a change of symmetry also be possible.



O=Ba, X=O, =Ti

Fig.13.5. Cubic lattice of Ba Ti O_3

This may be illustrated with a typical example of Ba Ti O_3 at high temperature. It has a cubic lattice (as shown in Fig.13.5) with Ba atoms at the vertices, O atoms at the centres of the faces and Ti atoms at the centres of the cells. As the temperature decreases below a certain value. Ti and O atoms begin to move relative to Ba atoms, parallel to edge of the cube. Due to this movement, the symmetry of the lattice changes, and it becomes tetragonal instead of cubic. In this process the configuration of the atoms in the crystal changes continuously. Such a transition from one crystal modification to another is called a second-order phase transition in contrast to the first order.



(a) (b)

O = Zn, = Cu

Fig.13.6. Body-centered cubic lattice of β-brass

The change in symmetry of the system takes place not only due to the displacement of atoms but also due to a change in the ordering of the crystal. Let us consider a specific example of β-brass at low temperature. It is a completely ordered alloy of Cu and Zn, which has a cubic lattice with Zn atoms at the vertices and Cu atoms at the centre of the cubic cell (Fig.13.6a). When the alloy is heated, it becomes disordered, and Cu and Zn atoms change places, i.e. there are probabilities of finding atoms of either kind at every lattice site until the probabilities of finding Cu(or Zn) atoms at the vertices and at the centres of the cells becomes equal. In this process, these sites remain nonequivalent and the symmetry of the lattice is unchanged. But the moment the probabilities become equal, all sites become equivalent and the symmetry of the crystal is raised. The crystal acquires a body-centred cubic Bravais lattice (Fig.13.6b). Such a crystal will be said to be disordered.

Since the states of two phases are the same at the transition point of the second kind, it is clear that the symmetry of the body at the transition point itself must contain all the symmetry elements of the phases.

We have considered the characteristic of a first-order phase transition in Sec.13.3 in which the internal energy and specific volume change discontinuously and heat is evolved or absorbed. However, the phase transition of the second order is accompanied by a smooth change of internal energy and specific volume. In the process of second-order phase transition no heat is evolved or absorbed.

Ehrenfest suggested the possibility of the second-order phase transition where the second derivative of G, the molar Gibbs function might be finite but different for the two phases 1 and 2 in equilibrium. Let us consider a phase change between two phases 1 and 2 in equilibrium at pressure P and temperature T and let

$$g = G_1 - G_2$$

Thus,

$$g(P, T) = 0 \tag{13.4.1}$$

We now change the temperature of each phase by dT and the pressure by dP, such that the two phases continue to be in equilibrium, then

$$g(P + dP, T + dT) = 0 \tag{13.4.2}$$

Making a Taylor-series expansion up to the second order, we have

$$g(P, T) + [(\partial g/\partial P)dP + (\partial g/\partial T)dT\,] + (1/2)\,[(\partial^2 g/\partial P^2)\,(dP)^2 + 2\,(\partial^2 g/\partial P \partial T)\,dP dT + (\partial^2 g/\partial T^2)\,(dT)^2\,] + \ldots = 0 \tag{13.4.3}$$

We know that the function g is always zero at equilibrium. If both $\partial g/\partial P$ and $\partial g/\partial T$ are finite, but the sum of the first order terms is zero, then we

$$(\partial g/\partial P)dP + (\partial g/\partial T)dT = 0 \tag{13.4.4}$$

which leads to (13.3.8). This corresponds to the first-order transition. However, when $\partial g/\partial P$ and $\partial g/\partial T$ are individually zero, we must consider the second order terms. When $\partial g/\partial P$ and $\partial g/\partial T$ are zero both at (P, T) and at (P+dP, T+dT), we have

$$\partial g/\partial P = (\partial^2 g/\partial P^2)\,dP + (\partial^2 g/\partial P \partial T)\,dT = 0 \tag{13.4.5}$$

$$\partial g/\partial T = (\partial^2 g/\partial T \partial P)\, dP + (\partial^2 g/\partial T^2)\, dT = 0 \qquad (13.4.6)$$

Adding (13.4.5) and (13.4.6) we find that the sum of the second order terms of (13.4.3) is zero, i.e.

$$(\partial^2 g/\partial P^2)\,(dP)^2 + 2(\partial^2 g/\partial P \partial T)dPdT + (\partial^2 g/\partial T^2)(dT)^2 = 0 \qquad (13.4.7)$$

This corresponds to a phase transition of the second order. If such an equality holds for an arbitrary dP and dT, the following conditions must be satisfied.

$$(\partial^2 g/\partial T^2) > 0$$

$$(\partial^2 g/\partial P^2) > 0 \qquad (13.4.8)$$

and

$$(\partial^2 g/\partial T^2)\,(\partial^2 g/\partial P^2) - (\partial^2 g/\partial P \partial T) > 0 \qquad (13.4.9)$$

From (13.4.8), we obtain

$$\partial^2 G_1/\partial T^2 \neq \partial^2 G_2/\partial T^2 \qquad (13.4.10a)$$

and

$$\partial^2 G_1/\partial P^2 \neq \partial^2 G_2/\partial P^2 \qquad (13.4.10b)$$

Using relation (13.3.6), we have

$$\partial^2 G/\partial T^2 = -(\partial s/\partial T)_P = -(C_P/T) \qquad (13.4.11a)$$

$$\partial^2 G/\partial P^2 = (\partial v/\partial P)_T \qquad (13.4.11b)$$

$$\partial^2 G/\partial T \partial P = (\partial v/\partial T)_P \qquad (13.4.11c)$$

Equations (13.4.5) and (13.4.6) give us two possible equations for the phase transition boundary, viz.

$$dP/dT = -(\partial(\Delta v)/\partial T)_P/(\partial(\Delta v)/\partial P)_T \qquad (13.4.12a)$$

and

$$dP/dT = (\partial(\Delta s)/\partial T)_P/(\partial(\Delta v)/\partial T)_P \qquad (13.4.12b)$$

where $\Delta s = s_2 - s_1$ and $\Delta v = v_2 - v_1$.

At a second order phase transition, not only the thermodynamic potentials are continuous, but their first derivatives $(\partial G/\partial P)_T$ and $(\partial G/\partial T)_P$ are also continuous, however, their second derivatives given in (13.4.11) undergo a jump. These characteristic of second order phase transition are shown in Fig.13.7.

Apart from well known liquid-gas phase transition of the first order, there are known examples of the second order, e.g. transition from liquid helium I to liquid helium II, where $C_v - T$ curve has a shape of λ. Another example of a λ transition is the order- disorder transformation in alloys, such as β-brass. It is important to note that in a first-order transition, C_P remains finite up to the transition point where it becomes infinity (see Fig.13.4) while in second-order transition (i.e. in a λ transition), C_P starts rising before the transition temperature is reached (see Fig.7.6).

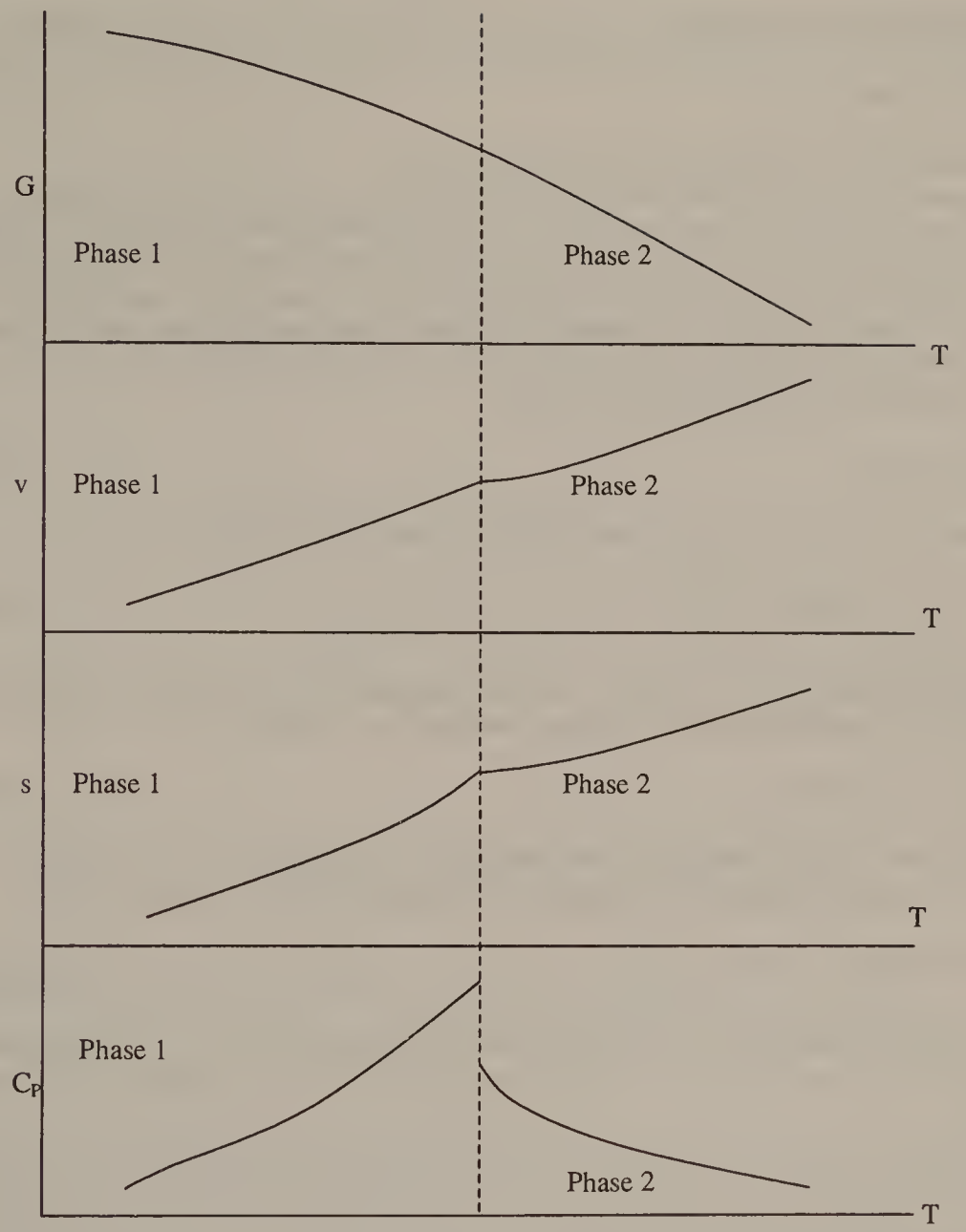


Fig.13.7. Variation of G, v, s and C_p during the second order transition

13.5. The Critical Indices

In Fig.1.2, the phase equilibrium curve may terminate at a certain point C, called the critical point. Beyond that point, no difference of phases exists. Thus, at the critical point the two phases become identical. At this point the isotherm has a point of inflexion satisfying

$$(\partial P/\partial \rho)_T = 0$$

$$(\partial^2 P/\partial \rho^2)_T = 0 \qquad (13.5.1)$$

From thermodynamics we can show that

$$-(1/C_v)(\partial P/\partial V)_T \geq 0 \qquad (13.5.2)$$

The critical point is defined as the point where the equality holds.

Many thermodynamic properties have anomalous values in the vicinity of the critical point. A basic problem in the theory of phase transition is to study the anomalous behaviour of a physical system near this point. These anomalies are the direct consequences of the large density fluctuations characteristic of the critical region. These fluctuations give rise to singularities usually expressed in terms of a set of critical indices. In the vicinity of the critical point, the property varies as a simple power of the temperature difference from the critical point. The singular behaviour of a physical quantity X is usually described by a simple power law

$$X \propto (T - T_c)^m \qquad (13.5.3)$$

where m is some positive number called a critical exponent, which is determined by

$$m = \lim_{T \to T_c} [\ln X / \ln(T - T_c)] \qquad (13.5.4)$$

The anomalous behaviour of a number of physical properties can be described by similar power laws. For example, we consider the isothermal compressibility K_T defined by

$$K_T = -(1/V)(\partial V/\partial P)_T \qquad (13.5.5)$$

which becomes infinity at the critical point. If the divergence is represented as a power law in $|T - T_c|$, then for $T > T_c$ the singular behaviour of K_T along the critical isochore ($\rho = \rho_c$) is represented by

$$K_T = A\,|T - T_c|^{-\gamma} \qquad T > T_c \qquad (13.5.6)$$

where γ is a positive constant, called a critical exponent. For insulating liquid, $\gamma \sim 1.1$. This equation is valid only in the immediate vicinity of the critical point. For $T < T_c$ the divergence of K_T can be represented by

$$K_T = A'\,|T - T_c|^{-\gamma'} \qquad T < T_c \qquad (13.5.7)$$

The critical exponent γ' is not necessarily equal to γ.

The asymptotic behaviour of other properties can also be described by similar power laws. Thus, the singular behaviour of the specific heat at constant volume C_v is represented by

$$C_v = B\,|T - T_c|^{-\alpha} \qquad T > T_c$$

$$= B'\,|T - T_c|^{-\alpha'} \qquad T < T_c \qquad (13.5.8)$$

However, C_v shows a weak divergence at the critical point, α and α' are the critical exponents in this case.

A property which goes to zero at the critical point gives rise to a power law similar to (13.5.6), but without the minus sign in the exponent. The difference between liquid and gas densities, which vanishes at the critical point is given by

$$\rho_l - \rho_g = C(T - T_c)^{\beta} \tag{13.5.9}$$

where $\beta = 0.345 \pm 0.015$ for insulating fluids.

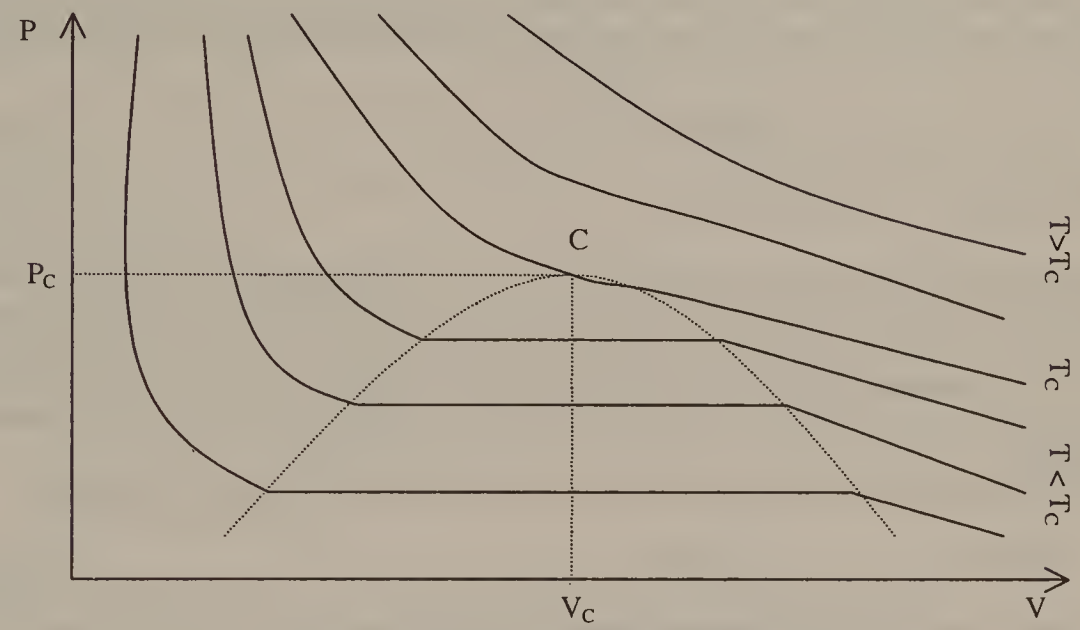


Fig.13.8. Isotherm for a liquid gas phase transition

In Fig.13.8, the critical isotherm (i.e. for $T = T_c$) is shown, which has a horizontal tangent at the critical point. If the portion of this line near the critical point is given by $P - P_c$, then

$$P - P_c = D(T - T_c)^{\delta} \tag{13.5.10}$$

where the critical exponent δ for insulating liquid is 4.35.

The above results demonstrate the way in which several thermodynamic properties are found to behave near the critical point. The numerical values of the critical exponents appear to be identical for all substances on which investigations have been made so far. Thus, the critical exponents are independent of the precise nature of the substance considered. This shows the universality of the critical point behaviour. The critical exponents above and below the critical temperature T_c are found to be the same, i.e.

$$\gamma = \gamma'$$

$$\alpha = \alpha' \tag{13.5.11}$$

The critical exponents are not all independent of each other. The laws of thermodynamics can be used to derive a number of rigorous inequalities between the combinations of the critical exponents. In particular, the Rushbrooke inequality (Rushbrooke 1963, 1965)

$$\alpha' + 2\beta + \gamma' \geq 2 \tag{13.5.12}$$

and the Griffiths inequality (Griffiths, 1965)

$$\alpha' + \beta(\delta + 1) > 2 \tag{13.5.13}$$

13.6. van der Waals Theory of Liquid Gas Transition

The van der Waals equation of state is the simplified model which predicts the qualitative features of the liquid-gas transition. We have discussed the van der Waals equation of state in detail in Sec.9.1. Equation (9.1.20) in terms of density ρ can be written as

$$P/kT = (\rho/(1 - b'\rho)) - (\rho^2 a'/kT) \tag{13.6.1}$$

where

$$b' = b/N \; ; \qquad a' = a/N^2$$

This equation predicts the critical behaviour of the P – V (or P-ρ) isotherms similar to those shown in Fig.9.2, which arises due to the hard-core repulsion of the molecules (represented by the excluded volume term b) as well as the long-range attraction between the molecules (represented by the pressure term a). For the two-phase region below the critical point, the shape of this curve is abnormal, but in the single phase region (i.e. in gas or liquid) it gives curves qualitatively similar to those observed experimentally.

The critical point for the van der Waals equation can be determined by the usual conditions

$$(\partial P/\partial \rho)_T = 0 \; ; \qquad (\partial^2 P/\partial \rho^2)_T = 0 \tag{13.6.2}$$

which can be solved to give the critical temperature T_c, critical pressure P_c and critical density ρ_c (or critical volume V_c). They were expressed in terms of the parameters a and b in Eq.(9.1.22), i.e.

$$T_c = 8a/27bNk \; ; \qquad P_c = a/27b^2 \; ; \qquad \rho_c = 1/3b \tag{13.6.3}$$

The van der Waals approximation for the attractive interaction is rigorous in the limit of weak long-range intermolecular force. However, in the real fluids the attractive forces are usually not long-range. This is the reason why this theory fails to represent the observed thermodynamic behaviour near the critical point.

The van der Waals equation is an example of a classical, or mean field equation of state where the pressure P is an analytic function of ρ and T. This theory can be used to estimate the critical exponents.

In order to estimate the critical exponents, the pressure $\Delta P \equiv P - P_c$ is expanded in a series in terms of the deviation $\Delta\rho \equiv \rho - \rho_c$

$$\Delta P = p_o(T) + p_1(T)\Delta\rho + p_2(T)(\Delta\rho)^2 + p_3(T)(\Delta\rho)^3 + \ldots \tag{13.6.4}$$

where $p_n(T)$ with n = 0, 1, 2, 3, ... are unknown functions of temperature. The form of $p_n(T)$ can be obtained from the result $\Delta P = 0$ when $T = T_c$. Hence, $p_n(T)$ can be further expanded in terms of $\Delta T \equiv T - T_c$ as

$$p_n(T) = p_{on}(T_c) + p_{1n}\Delta T + p_{2n}(\Delta T)^2 + \ldots \tag{13.6.5}$$

We now consider the coefficients $p_n(T)$ for n = 0, 1, 2, 3, … . Since $\Delta P = 0$ when $T = T_c$.

$$p_{oo}(T_c) = 0$$

In the limit $\Delta T = 0$ (i.e. at $T = T_c$), we find that

$$\Delta P/\Delta\rho = (\partial P/\partial\rho)_{T=T_c} \to 0$$

so that

$$p_{o1}(T_c) = 0$$

Since the pressure P is considered to be a function of ρ, we have for $T = T_c$

$$\Delta P = (\partial P/\partial\rho)_{T_c}\Delta\rho + (\partial^2 P/\partial\rho^2)_{T_c}(\Delta\rho)^2 + (\partial^3 P/\partial\rho^3)_{T_c}(\Delta\rho)^3 + \ldots \quad (13.6.6)$$

As $(\partial^2 P/\partial\rho^2)_{T_c} = 0$, $p_{o2}(T) = 0$. However $(\partial^3 P/\partial\rho^3)_{T_c} \neq 0$, hence $\Delta P \propto (\Delta\rho)^3$ and $p_{03} \neq 0$. Expansion of $p_n(T)$ can be given by

$$p_0(T) = p_{10}\Delta T + p_{20}(\Delta T)^2 + \ldots$$

$$p_1(T) = p_{11}\Delta T + p_{21}(\Delta T)^2 + \ldots$$

$$p_2(T) = p_{12}\Delta T + p_{22}(\Delta T)^2 + \ldots$$

$$p_3(T) = p_{03} + p_{13}\Delta T + \ldots$$

Substituting these values in (13.6.4) and retaining the lowest order terms, we get

$$\Delta P = p_{10}\Delta T + p_{11}\Delta T\Delta\rho + p_{12}\Delta T(\Delta\rho)^2 + p_{03}(\Delta\rho)^3 + \ldots \quad (13.6.7)$$

Along the critical isotherm, $\Delta T = 0$ and at $T = T_c$

$$\Delta P = (P - P_c) = p_{03}(\Delta\rho)^3 \quad (13.6.8)$$

Thus, $\delta = 3$, showing that the critical isotherm is cubic in form. Now it follows from (13.6.7) that

$$p_{03}(\Delta\rho)^2 \quad (\Delta P/\Delta\rho) - p_{10}(\Delta T/\Delta\rho) - p_{11}\Delta T \quad (13.6.9)$$

As $T \to T_c$ (i.e. $\Delta T \to 0$), we find that

$$\Delta P/\Delta\rho = (\partial P/\partial\rho)_{T_c} = 0$$

$$\Delta T/\Delta\rho = (\partial T/\partial\rho)_{P_c} = -(\partial P/\partial\rho)_{T_c}/(\partial P/\partial T)_{\rho_c} = 0 \quad (13.6.10)$$

since

$$(\partial P/\partial T)_{\rho_c} = \Delta P/\Delta T$$

which is finite at the critical point. Thus (13.6.9) reduces to

$$\Delta\rho = (-p_{11}/p_{03})^{1/2}(\Delta T)^{1/2} = C(\Delta T)^{1/2} \quad (13.6.11)$$

Hence we find that $\beta = \frac{1}{2}$ in this theory.

From (13.6.9), we can calculate $((\partial P/\partial T)_T$ near the critical point. Thus

$$(\partial P/\partial T)_T = \Delta P/\Delta\rho = p_{11}\Delta T + p_{03}(\Delta\rho)^2 \tag{13.6.12}$$

Along the critical isochore, $\Delta\rho$ is zero, and the isothermal compressibility at the critical density ρ_c is given by

$$K_T = (1/\rho)\,(\partial\rho/\partial P)_T = (1/p_{11}\rho_c)\,(\Delta T)^{-1} \tag{13.6.13}$$

giving $\gamma = 1$ in reasonable agreement with experiment.

The critical exponents obtained by the van der Waals theory do not depend on the explicit form of the equation of state. They are a direct consequence of the assumption that the equation of state is an analytic function of ρ and T in the immediate neighbourhood of the critical point. They can be obtained by expanding the equation of state in a Taylor series in terms of $\Delta\rho$ and ΔT. However, these theoretical results disagree with experiment. Hence, a Taylor expansion at the critical point is not possible.

13.7. Mayer Theory of Condensation

In this section, we employ the Mayer theory of cluster expansions, developed in Sec.9.2, to predict some features of liquid-gas transition of a system.

According to Mayer theory, the partition of an N-particle classical system is given by Eq.(9.2.17) i.e.

$$Q_N = (1/\lambda^{3N}) \sum_{(m_l)} [\prod_l (Vb_l)^{m_l}/m_l!] = \sum_{(m_l)} [\prod_l (Vb_l/\lambda^{3l})^{m_l}/m_l!] \tag{13.7.1}$$

where b_l's are the cluster integrals, defined by (9.2.9) and summation Σ goes over all sets m_l with the condition

$$\sum_{l=1}^{N} l m_l = N, \quad m_l = 0, 1, 2, \ldots, N \tag{13.7.2}$$

m_l's denote the number of cluster of various size. At high temperatures, large-sized clusters ($l >> 1$) will not be present in significant numbers. When the temperature decreases, a critical stage is reached when large-sized cluster are formed suddenly. This stage may be identified with the condensation point of the system. Let us find out this point.

Let us select the largest term from the sum(13.7.1) with the maximal set $\{m_l^*\}$. Then lnQ is asymptotically equal to the logarithm of this term. Thus we have

$$\ln Q = \ln [\prod_l (Vb_l/\lambda^{3l})^{m_l^*}] - [m_l^* \ln m_l^* - m_l^*] = \sum_l m_l^* [\ln ((Vb_l/\lambda^{3l}) - \ln m_l^* + 1] \tag{13.7.3}$$

lnQ must be maximum. Hence

$$\delta \ln Q = 0 \tag{13.7.4}$$

We use condition to determine m_l^*. Substituting (13.7.3) in (13.7.4), we get

$$\sum_l [\ln (Vb_l/\lambda^{3l}) - \ln m_l^*] \, \delta m_l^* = 0 \tag{13.7.5}$$

From (13.7.2)

$$\sum_l l \delta m_l^* = 0 \tag{13.7.6}$$

Using Lagrange's method of undetermined multiplier, where (13.7.6) is multiplied by α and substracted from (13.7.5), we obtain

$$\sum_l [\ln (Vb_l/\lambda^{3l}) - \ln m_l^* - \alpha l] \, \delta m_l^* = 0$$

This is possible when

$$\ln (Vb_l/\lambda^{3l}) - \ln m_l^* - \alpha l = 0$$

or

$$m_l^* = (V/\lambda^{3l}) \, b_l \exp(-\alpha l) \tag{13.7.7}$$

Substituting (13.7.7) in (13.7.3), we get

$$\ln Q = \sum_l m_l^* (\alpha l + 1) = \alpha N + \sum_l (V/\lambda^{3l}) \, b_l \exp(-\alpha l) \tag{13.7.8}$$

From (13.7.2), we have

$$\rho = N/V = \sum_l l m_l^* = \sum_l (l b_l/\lambda^{3l}) \exp(-\alpha l)$$

Comparing it with (9.2.24), we

$$\alpha = -\ln z'$$

Then (13.7.7) becomes

$$m_l^* = (V/\lambda^{3l}) \, b_l \, z'^l = V b_l z^l \tag{13.7.9}$$

which gives with the help of (9.2.23)

$$\beta P = \sum_{l \geq 1} m_l^* \tag{13.7.10}$$

Thus the imperfect gas composed of real particles may be assumed as a 'perfect gas mixture' of different sized cluster in equibrium with one-another.

Let us now study the behaviour of the number m_l^* for large values of l. For this purpose we can express the cluster integral b_l in terms of the irreducible cluster integral β_k by (9.2.35) viz

$$b_l = (1/l^2) \sum_{n_k} \left[\prod_{k=1}^{l-1} (l\beta_k)^{n_k}/n_k! \right] \tag{13.7.11}$$

where β_k's are the irreducible cluster integrals, while the summation Σ goes over all the sets $\{n_k\}$ which satisfies the condition

$$\sum_{k=1}^{l-1} k n_k = l - 1 \tag{13.7.12}$$

For large l, the number $\ln b_l$ will be very nearly equal to the logarithm of the largest term in the sum (13.7.11), i.e

$$\ln b_l = -2 \ln + \sum_{k=1}^{l-1} n_k^* \{\ln(l\beta_k) - \ln n_k^* + 1\} \tag{13.7.13}$$

In this case n_k^*'s are determined by the conditions

$$\sum_k [\ln(l\beta_k) - \ln n_k^*] \delta n_k = 0 \tag{13.7.14a}$$

and

$$\sum_k k \delta n_k^* = 0 \tag{13.7.14b}$$

Again, using the Lagranges method of undetermined multiplier, we get

$$\ln (l\beta_k) - \ln n_k^* - \gamma k = 0$$

or

$$n_k^* = l\beta_k \exp(-\gamma k) \tag{13.7.15}$$

where γ is the undetermined multiplier. Substituting (13.7.15) in (13.7.12), we get

$$\sum_k k\beta_k \exp(-\gamma k) = (l-1)/l \approx 1 \tag{13.7.16}$$

Eq.(13.7.16) determines the value of γ.

Now substituting (13.7.15) in (13.7.13), we get

$$\ln b_l \approx -2\ln l + \sum_k n_k^* (\gamma k + 1) = -2\ln l + (l-1)\gamma + l \sum_k \beta_k \exp(-\gamma k)$$

$$\approx l \left[\gamma + \sum_k \beta_k \exp(-\gamma k) \right] \tag{13.7.17}$$

Thus, we conclude that for large value of l, b_l can be expressed as

$$b_l = c_l b_0^l \tag{13.7.18}$$

where

$$b_0 = \exp \left[\gamma + \sum_k \beta_k \exp(-\gamma k)\right] \tag{13.7.19}$$

The factor c_l in (13.7.18) is also a function of the variable l.

Substituting (13.7.18) in (13.7.9) we obtain expression of the large sized cluster as

$$m_l^* = V c_l (b_0 z)^l \qquad (13.7.20)$$

where $b_0 z < 1$ and $l \gg 1$, m_l^* is practically equal to zero. On the other hand if $b_0 z > 1$, then m_l^* becomes exceeding large. Thus as z increases and becomes equal to the critical value $z_c = b_o^{-1}$, a large-sized cluster is suddenly formed.

The specific volume v is expressed by (9.2.24) i.e.

$$(1/v) = \sum_k l\, b_l z^l \qquad (13.7.21)$$

Substituting $z = b_o^{-1}$, the critical value v_c, at which a sudden formation of large sized cluster takes place, is given by

$$(1/v_c) = \sum_{l \geq 1} l\, b_0\, b_o^{-1} \qquad (13.7.22)$$

The variation of fugacity z as a function of the specific volume v in the region of gas-liquid transition is shown in Fig.13.9. The horizontal portion represents the formation of large-sized cluster and hence the appearance of a two phase state in the system.

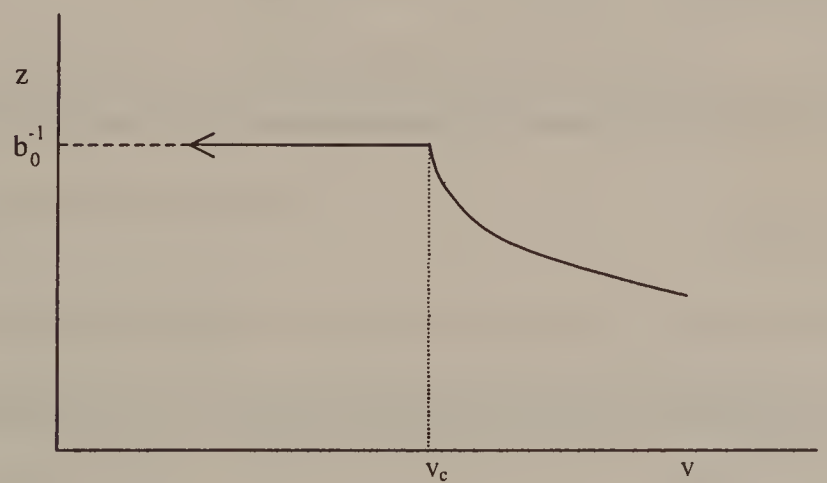


Fig.13.9. Fugacity z as a function of the specific volume v in the region of gas liquid transition

13.8. Curie-Weiss Theory of Magnetic Transition

In this section we consider the magnetic transition. Thermodynamically the descriptions of the magnetic transition are almost identical to that of the corresponding transition for gaseous system. However, there are simplifying features for magnets.

When a magnetic field **B** is applied to some metal, e.g., Fe and Ni (in a particular direction) at sufficiently low temperature $T(T < T_c)$, the metal gets a magnetisation $\langle M(\mathbf{B},T)\rangle$. Then the field is turned off. However, a residual or spontaneous magnetisation $M_o(T) = \langle M(0,T)\rangle$ remains as long as $T < T_c$. When $T > T_c$, there is no spontaneous magnetisation and M_0 vanishes abruptly at $T \to T_c$. This is due to the fact that a finite fraction of the spins of the atoms becomes spontaneously oriented in the

same direction at $T < T_c$, giving rise to a magnetic field. At $T > T_c$, the spins are oriented at random producing no resultant magnetic field. The transition from a spontaneous magnetisation for $T < T_c$ to no magnetisation for $T > T_c$ may be interpreted as a ferromagnetic phase transition with Curie temperature T_c. The phenomenon of ferromagnetism is associated only with the spins of the electrons, and not with their orbital motion.

Let us consider a system consisting of an array of N lattice sites, each occupied by an atom possessing a magnetic moment $\mu = 2\mu_B s$, where s is the spin variable associated with a lattice site. Since $s = \pm 1/2$, only two orientation are possible for each site. The interaction energy between spins i and j is given by

$$\in_{ij} = \text{const.} - 2J_{ij}(s_i.s_j) \tag{13.8.1}$$

where J_{ij} is the exchange energy between them, which is negligible except for the nearest-neighbouring pairs. When $J_{ij} > 0$, we get the lowest possible energy for a state of parallel spins. This corresponds to a ferromagnetic system. On the other hand, when $J_{ij} < 0$, we get the lowest energy for a state of antiparallel spins. This corresponds to an antiferromagnetic system. For simplicity, we consider the case of isotropic interaction so that $J_{ij} = J$ for all i, j. Thus, the interaction energy of system is given by

$$E = \text{const.} - 2J \sum_{(n,n)} (s_i.s_j) \tag{13.8.2}$$

where the summation goes over all the nearest-neighbour pairs in the lattice. This model is known as the Heisenberg model of ferromagnetism.

13.9. Ising Model

A simpler model is introduced by Ising who assumes that the quantisation takes place along the z-axis and replace the product $(s_i.s_j) = (s_{ix}s_{jx} + s_{iy}s_{jy} + s_{iz}s_{jz})$ by a single term $s_{iz}s_{jz}$. Under this approximation, (13.8.2) may be written as

$$E = \text{const.} - J \sum_{(n,n)} \sigma_i.\sigma_j \tag{13.9.1}$$

where σ_i (or σ_j) = +1 for an up spin and –1 for a down spin. This simpler model is known as the *Ising model* of ferromagnetism.

In the presence of the external magnetic field **B**, the spins possess an additional potential energy, given by $-\mu B\sigma_i$. Then the Hamiltonian of the system in configuration $\{\sigma_i, \sigma_2, \ldots, \sigma_N\}$ is given by

$$H\{\sigma_i\} = -J \sum_{(n,n)} \sigma_i.\sigma_j - \mu B \sum_i \sigma_i \tag{13.9.2}$$

This produces a magnetic moment, resulting in ferromagnetism only when $J > 0$.

The partition function is given by

$$Q_N(B,T) = \sum_{\{\sigma_i\}} \exp[-\beta H(\sigma_i)] = \sum_{\{\sigma_i\}} \exp[\beta J \sum_{n.n} \sigma_i.\sigma_j + \beta\mu B \sum_i \sigma_i] \tag{13.9.3}$$

where each σ_i ranges independently over the values ± 1. Hence there are 2^N terms in the summation.

Then the Helmholtz free energy of the system is given by

$$A(B, T) = -kT \ln Q_N(B,T) \tag{13.9.4}$$

Other thermodynamic functions, such as the internal energy, the specific heat and the magnetisation are obtained in the usual manner from the Helmholtz free energy

$$U(B, T) = -T^2(\partial/\partial T)\,(A/T) \tag{13.9.5}$$

$$C(B, T) = (\partial U/\partial T) \tag{13.9.6}$$

$$\langle M(\mathbf{B},T)\rangle = \langle -(\partial H/\partial B)\rangle = (\partial A/\partial B)_T = \mu \langle \sum_i \sigma_i \rangle \tag{13.9.7}$$

The quantity $\langle M(0,T)\rangle$ is called the spontaneous magnetisation. If it is non-zero, the system in said to be ferromagnetic for $T < T_c$ and paramagnetic for $T > T_c$.

The energy levels (13.9.2) is, in general, degenerate. Although a configuration of the system is specified by the N numbers $\sigma_1, \sigma_2, \ldots, \sigma_N$, the energy of a given configurations $\{\sigma_i\}$ does not depend upon the detailed values of the variables σ_i, it only depends upon the nearest neighbours. Let N_+ be the total number of the "up" spins and N_- the total number of the "down" spin such that

$$N_+ + N_- = N \tag{13.9.8}$$

Let N_{++}, N_{--} and N_{+-} be the total number of the "up-up", "down-down" and "up-down" neighbour pairs respectively, where $N_{+-} = N_{-+}$. If γ is the number of nearest neighbours, where

$$\gamma = \begin{cases} 4 & \text{(two-dimensional square lattice)} \\ 6 & \text{(three-dimensional simple cubic lattice)} \\ 8 & \text{(three-dimensional body-centered cubic lattice)} \end{cases}$$

then we have the following relations

$$\begin{aligned} \gamma N_+ &= 2N_{++} + N_{+-} \\ \gamma N_- &= 2N_{--} + N_{+-} \end{aligned} \tag{13.9.9}$$

With the help of Eqs.(13.9.8) and (13.9.9), we can express any two of them, say, N_+ and N_{++} as

$$\begin{aligned} N_- &= N - N_+ \\ N_{+-} &= \gamma N_+ - 2N_{++} \\ N_{--} &= (1/2)\gamma N - \gamma N_+ + N_{++} \end{aligned} \tag{13.9.10}$$

Naturally, it can be written as

$$\sum_{i=1} \sigma_i = N_+ - N_- = 2N_+ - N \tag{13.9.11a}$$

$$\sum_{(n,n)} \sigma_i.\sigma_j = N_{++} + N_{--} - N_{+-} = 4N_{++} - 2\gamma N_+ + (1/2)\gamma N \tag{13.9.11b}$$

Substituting (13.9.11) in (13.9.2), we get

$$H_N(N_+, N_{++}) = -J(4N_{++} - 2\gamma N_+ + (1/2)\gamma N) - \mu B(2N_+ - N)$$

$$= N((1/2)J\gamma - \mu B) + 2(J\gamma - \mu B)N_+ - 4JN_{++} \qquad (13.9.12)$$

Thus in the Ising model, the energy of a state depends on the number N_+ and N_{++}. Then the partition function of the system can be written as

$$Q_N(B,T) = \exp(\beta N((1/2)J\gamma - \mu B)) \sum_{N_+=0}^{N} \exp(-2\beta(J\gamma - \mu B)N_+) \sum'_{N_{++}} g(N_+, N_{++}) e^{4\beta J N_{++}} \qquad (13.9.13)$$

where $g(N_+, N_{++})$ is the number of configurations which have a given set of the numbers N_+ and N_{++}. The primed sum Σ' goes over all values of N_{++} which are consistent with a fixed value of N_+, and a summation over all possible values of N_+. Since $g(N_+, N_{++})$ is a complicated function, the calculation of (13.9.13) is not simple.

13.10. Ising Model in the Zeroth Approximation

We assume that the range of interaction is very long, so for most configurations, each spin effectively interacts with a mean field produced by other spins. Under this approximation the energy of the system does not depend on the detailed structure of the lattice but only on the numbers N_+ and N_{++}. Hence this approximation is called the zeroth approximation.

We define the long range order parameter L as

$$N_+ = (N/2)(1 + L)$$

$$N_- = (N/2)(1 - L) \qquad (-1 < L < +1) \qquad (13.10.1)$$

Then the magnetisation <M> is given by

$$<M> = (N_+ - N_-)\mu = N\mu L \qquad (13.10.2)$$

and the parameter L is a direct measure of magnetisation per particle.

We further define the short range order parameter α as

$$(N_{++}/(1/2)\gamma N) = (1/2)(\alpha + 1) \qquad (-1 < \alpha < 1) \qquad (13.10.3)$$

Substituting (13.10.1) and (13.10.3) in (13.9.11), we obtain

$$\sum_{i=1}^{N} \sigma_i = NL$$

$$\sum_{n,n} \sigma_i.\sigma_j = (1/2)\,\gamma N\,(2\alpha - 2L + 1) \qquad (13.10.4)$$

Then (13.9.2) is expressed in the form

$$H_N(L, \alpha) = -(1/2)J\gamma N\,(2\alpha - 2L + 1) - \mu BNL \qquad (13.10.5)$$

Now according to the Bragg-Williams approximation, the short-range order always follows from long-range order, which leads to

$$(N_{++}/(1/2)\gamma N) \quad (N_+/N)^2$$

or

$$\alpha \quad (1/2)(L+1)^2 - 1 \tag{13.10.6}$$

In this approximation, the Hamiltonian of the system becomes

$$H_N(L) \quad -N((1/2)J\gamma L^2 + \mu BL) \tag{13.10.7}$$

and the partition function (13.9.3) is written as

$$Q_N(B,T) = \sum_{\{\sigma_i\}} \exp(\beta N((1/2)\, J\gamma L^2 + \mu BL)) \tag{13.10.8}$$

where the summation extends over all sets $\{\sigma_i\}$. Let us calculate the number of sets $\{\sigma_i\}$. From (13.10.1) it is evident that L is determined from N_+. The number of sets $\{\sigma_i\}$ is the number of distinct ways in which N_+ can be selected from N. Thus, this number is given by

$$N!/N_+!(N-N_+)! = N! / [(1/2)N(1+L)]!\,[(1/2)N(1-L)]!$$

and hence (13.10.8) takes the form

$$Q_N(B,T) = \sum_{L=1}^{+1} (N! / [(1/2)N(1+L)]!\,[(1/2)N(1-L)]!)\exp(\beta N((1/2)\, J\gamma L^2 + \mu BL)) \tag{13.10.9}$$

When $N \to \infty$, the logarithm of Q_N is equal to the logarithm of the largest term in the summand of (13.10.9). Using Stirling formula,

$$\ln N! = N \ln N - N$$

we obtain

$$\ln Q_N = \beta N((1/2)J\gamma \bar{L}^2 + \mu B\, \bar{L}) - N((1+\bar{L})/2)\ln((1+\bar{L})/2) - N((1-\bar{L})/2)\ln((1-\bar{L})/2) \tag{13.10.10}$$

where $\bar{L}$ is the value of L which makes the summand of (13.10.10) maximum. The value of $\bar{L}$ is obtained from the condition

$$\partial \ln Q_N/\partial \bar{L} = \beta N(J\gamma \bar{L} + \mu B) - (1/2)N \ln((1+\bar{L})/(1-\bar{L})) = 0$$

or

$$(1/2)\ln((1+\bar{L})/(1-\bar{L})) = \tanh^{-1}\bar{L} = \beta(J\gamma \bar{L} + \mu B) \tag{13.10.11}$$

or

$$\bar{L} = \tanh((J\gamma \bar{L} + \mu B)/kT) \tag{13.10.12}$$

which is precisely the equation that determines mean field $\bar{L}$ in the Curie-Weiss theory.

In case of spontaneous magnetisation where B = 0, (13.10.12) reduces to

$$\bar{L} = \tanh((J\gamma \bar{L} / kT) \tag{13.10.13}$$

This equation may be solved graphically as shown in Fig.13.10. For any temperature T, the value of $\bar{L}(T)$ is determined by the point of interaction of the straight line $\gamma = \bar{L}$ and the curve $y = \tanh(J\gamma \bar{L}/kT)$. We have the following solutions of Eq.(13.10.13)

$$\bar{L} = \begin{cases} \pm \bar{L}_0 & ((J\gamma/kT) > 1) \\ 0 & \\ \bar{L} = 0 & ((J\gamma/kT) < 1) \end{cases} \tag{13.10.14}$$

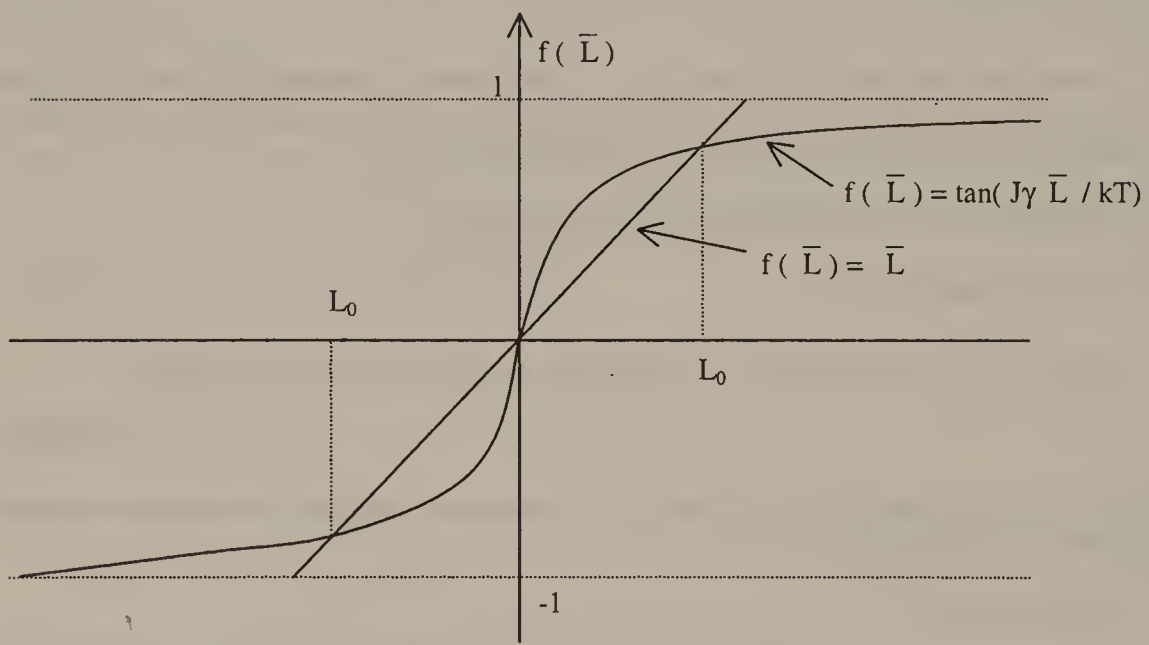


Fig.13.10. Graphical solution of Eq.(13.10.13)

However, in the first case we are primarily interested in the non-zero solution $\pm L_0$, which maximise the summand of (13.10.10). If $J > 0$, there exist a critical temperature T_c defined by

$$T_c = J\gamma/k \tag{13.10.15}$$

such that

$$\begin{aligned} \bar{L} &= \pm L_0 && (T < T_c) \\ &= 0 && (T > T_c) \end{aligned} \tag{13.10.16}$$

From (13.10.2), the spontaneous magnetisation per spin m_0 is given by

$$m_0 = \lim_{B \to 0} < M(B,T) > / N = \mu L_0 \qquad (13.10.17)$$

where L_0 is the solution of

$$L_0 = \tanh (J\gamma L_0/kT) \qquad (13.10.18)$$

In the vicinity of $T = T_c$, L_0 is small and we can write (13.10.18)

$$L_0 \quad (J\gamma L_0/kT) - (1/3)(J\gamma L_0/kT)^3 + \ldots$$

or

$$L_0^2 \quad 3(1 - (T/T_c))\,(T/T_c)^2$$

which gives

$$L_0 = [\,3(1 - (T/T_c))\,]^{1/2} \quad \text{as } T \to T_c \qquad (13.10.19)$$

On the other hand, when $T \to 0$, $L_0 \to 1$ and (13.10.18) can be expressed as

$$L_0 = (1 - \exp(-2T_cL_0/T)) / (1 + \exp(-2T_cL_0/T)) = 1 - 2\exp(-2T_cL_0/T) + \ldots$$

giving

$$L_0 = 1 - 2\exp(-2T_c/T) \quad \text{as } (T/T_c) \ll 1 \qquad (13.10.20)$$

The variation of L_0 with T is shown in Fig.13.11

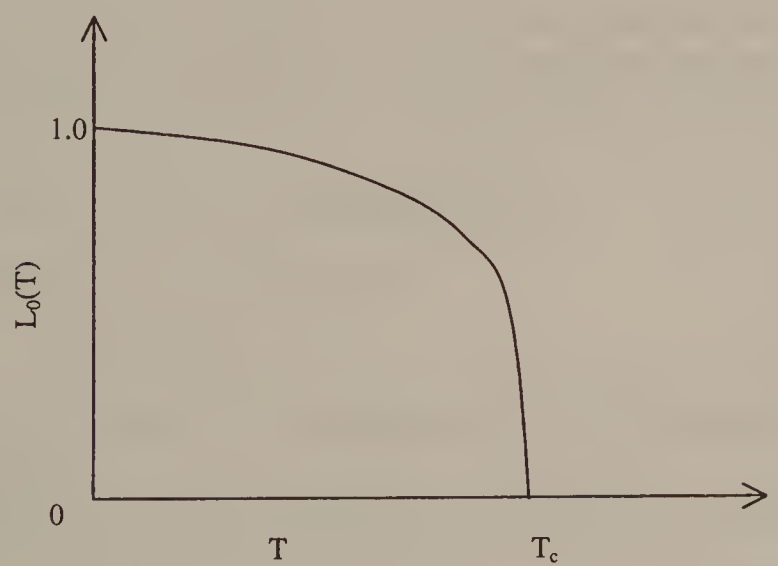


Fig.13.11. Variation of L_0 with T

The spontaneous magnetisation per spin from (13.10.17) is given by

$$m_0 = \mu [3(1 - (T/T_c))]^{1/2} \qquad (T < T_c)$$

$$= 0 \qquad (T > T_c) \qquad (13.10.21)$$

which is demonstrated in Fig.13.12

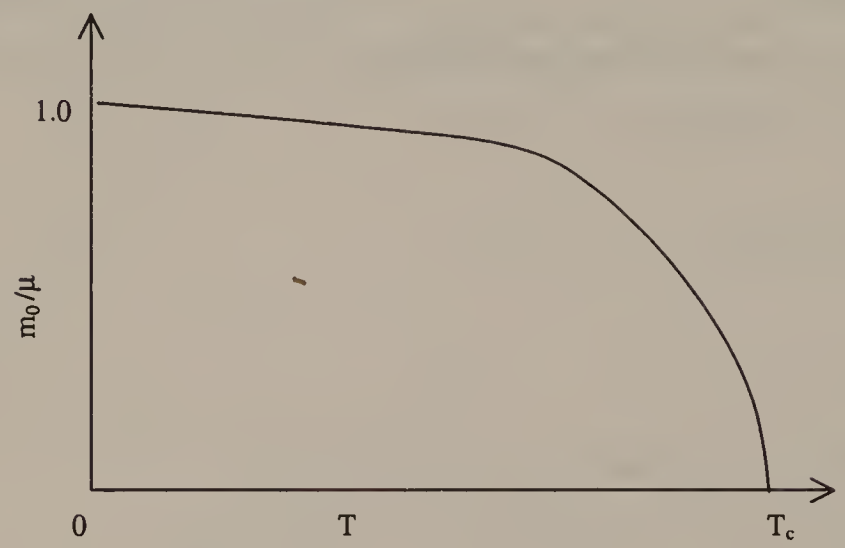


Fig.13.12. The spontaneous magnetisation per spin in the Bragg-Williams approximation

The zero field free energy is

$$A_0(T)/NkT = A(0,T)/NkT = -\ln 2 \qquad (T > T_c)$$

$$= -\ln 2 + (J\gamma/2kT)\, L_0^2 + (1/2) \ln (1 - L_0^2) \qquad (T < T_c) \qquad (13.10.22)$$

The zero-field internal energy is

$$U_0(T) \equiv U(0,T) = 0 \qquad (T > T_c)$$

$$= -(1/2)\, NJ\gamma L_0^2 \qquad (T < T_c) \qquad (13.10.23)$$

and the zero-field specific heat is,

$$C_0(T) \equiv C(0,T) = 0 \qquad (T > T_c)$$

$$= -NJ\gamma L_0 (\partial L_0/\partial T) \qquad (T < T_c) \qquad (13.10.24)$$

Using (13.10.19) we obtain C_0 at $T = T_c$

$$C_0(T_c) = (3/2)\, Nk$$

On the other hand, when (13.10.20) is used, the low temperature expression for C_0 is

$$C_0 \quad 4Nk(T_c/T)^2 \exp(-2T_c/T)$$

giving

$$C_0 \to 0 \text{ when } T \to o.$$

The variation of C_0 with T is shown in Fig.13.13. Below T_c, the specific heat increases with increase in temperature, and above T_c, it vanishes.

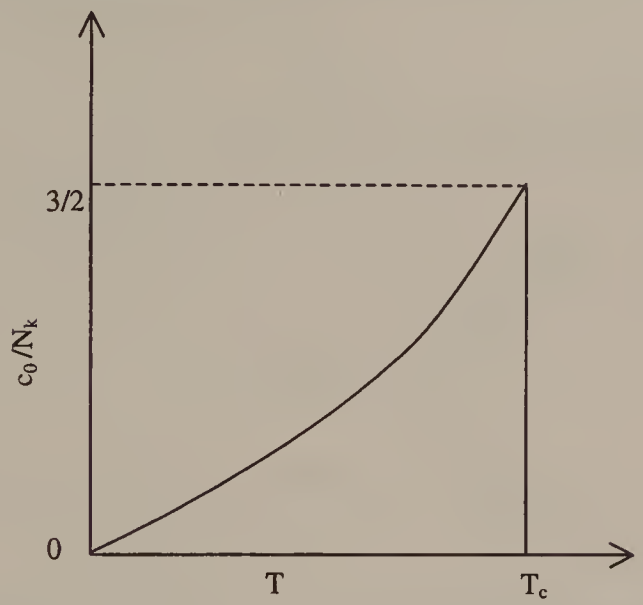


Fig.13.13. Zero-field specific heat C_0 of a Weiss ferromagnet as a function of temperature T

It is interesting to note that the thermodynamic quantities, such as magnetisation, internal energy, and specific heat of the system at zero-field, vanish for temperature above T_c. This is a consequence of the fact that the configurational order which prevails in the system at low temperatures is completely lost at $T \to T_c$.

We now consider the magnetic susceptibility of the system at high temperature ($\bar{L} \ll 1$) where the magnetic field **B** is not zero. Then (13.10.12) gives

$$\bar{L} \approx (J\gamma\bar{L} + \mu B)/kT$$

or

$$\bar{L} \approx \mu B/k(T - T_c) \qquad (13.10.25)$$

whence we obtain an expression for the isothermal magnetic susceptibility (per unit volume) of the system as

$$\chi_T = (\partial/\partial B)\,[<M>/V] = (N\mu/V)\,(\partial\bar{L}/\partial B) = N\mu^2/Vk(T - T_c) = C/(T - T_c) \qquad (13.10.26)$$

where

$$C = N\mu^2/Vk \qquad (13.10.27)$$

This is the famous Curie-Weiss law for the paramagnetic susceptibility of a ferromagnetic substance. However, it differs from the Curie law in which T is used instead of $(T - T_c)$.

13.11. Exact Solution of One-Dimensional Ising Model

The one dimensional Ising model is one of very few models in statistical mechanics, which are exactly solvable. The one-dimensional Ising model is a chain of N spins, each spin interacting only with its two nearest neghobours and with an external magnetic field.

We assume that the N th spin is connected to the first, so that the chain form a ring as shown in Fig.13.14. Then the Hamiltonian of the system in the configuration $\{\sigma_1, \sigma_2, \ldots, \sigma_N\}$ is given by

$$H = -J \sum_{i=1}^{N} \sigma_i \sigma_{i+1} - \mu B \sum_{i=1}^{N} \sigma_i$$

We impose the periodic boundary condition $\sigma_{N+1} = \sigma_1$, then H can be rewritten as

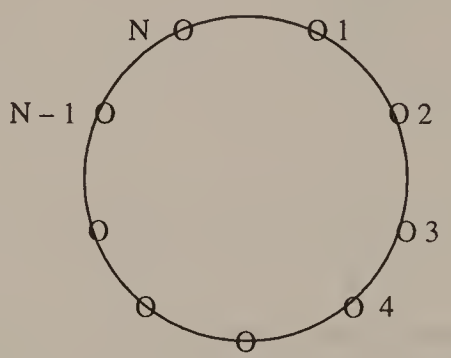


Fig.13.14. The one dimensional Ising chain model

$$H = -\sum_{i=1}^{N} [J \sigma_i \sigma_{i+1} + (1/2)\, \mu B\, (\sigma_i + \sigma_{i+1})] \qquad (13.11.1)$$

The partition function is

$$Q_N(B,T) = \sum_{\{\sigma_i\}} \exp[-\beta H]$$

$$= \sum_{\{\sigma_i\}} \exp[\beta \sum_{i=1}^{N} \{J \sigma_i \sigma_{i+1} + (1/2)\, \mu B\, (\sigma_i + \sigma_{i+1})\}]$$

$$= \sum_{\{\sigma_i\}} \prod_{i=1}^{N} \exp[\beta \{J \sigma_i \sigma_{i+1} + (1/2)\, \mu B\, (\sigma_i + \sigma_{i+1})\}] \qquad (13.11.2)$$

It is convenient to introduce the 2 x 2 transfer matrix P being so defined that its matrix elements are given by

$$\langle \sigma | P | \sigma' \rangle = \exp[\beta \{J \sigma\sigma' + (1/2)\, \mu B(\sigma + \sigma')\}] \qquad (13.11.3)$$

where σ and σ' may independently have the values ± 1, so all the matrix elements are

$$\langle +1 |P| +1\rangle = \exp [\, \beta(J+(1/2)\,\mu B)\,]$$

$$\langle -1 |P| -1\rangle = \exp [\, \beta(J-(1/2)\,\mu B)\,]$$

$$\langle +1 |P| -1\rangle = \langle -1 |P| +1\rangle = \exp [-\beta J]$$

Thus an explicit presentation P is

$$P = \begin{bmatrix} \exp [\, \beta(J + (1/2)\mu B)\,] & \exp(-\beta J) \\ \exp(-\beta J) & \exp [\, \beta(J+(1/2)\,\mu B)] \end{bmatrix} \qquad (13.11.4)$$

Then we may rewrite (13.11.2) in the form

$$Q_N(B,T) = \sum_{\sigma_1} \sum_{\sigma_2} \ldots \sum_{\sigma_N} \langle \sigma_1|P|\sigma_2\rangle \langle \sigma_2|P|\sigma_3\rangle \ldots \langle \sigma_N|P|\sigma_1\rangle$$

$$= \sum_{\sigma_1} \langle \sigma_1|P^N|\sigma_1\rangle = T_r P^N \qquad (13.11.5)$$

The matrix P has the eigen values λ_1 and λ_2 which are the roots of the secular determinant

$$|P - \lambda I| = 0 \qquad (13.11.6)$$

Solution of (13.11.6) is

$$\lambda_{1,2} = e^{\beta j} \cosh(\beta\mu B) \pm [e^{2\beta J} \sinh^2(\beta\mu B) + e^{-2\beta J}\,]^{1/2} \qquad (13.11.7)$$

where $\lambda_1 \geq \lambda_2$.
Similarly, the matrix P^N has the eigen values λ_1^N and λ_2^N. Hence

$$Q_N(B, T) = \lambda_1^N + \lambda_2^N \qquad (13.11.8)$$

Thus the Helmholtz free energy per spin is given by

$$A_N(B,T)/N = -(1/N\beta) \ln Q_N(B,T) = -(1/N\beta) \ln (\lambda_1^N + \lambda_2^N)$$

$$= -(1/N\beta) [N \ln\lambda_1 + \ln(1 + (\lambda_2/\lambda_1)^N\,] = -(1/\beta) \ln\lambda_1 \qquad (13.11.9)$$

as $N \to \infty$

Substituting the value of λ_1 from (13.11.7), we can write the Helmholtz free energy as

$$A(B,T) = -NKT \ln [e^{\beta J} \cosh(\beta\mu B) + (e^{2\beta J} \sinh^2(\beta\mu B) + e^{-2\beta J}\,)^{1/2}\,] \qquad (13.11.10)$$

For the special case B = 0, (13.11.10) reduces to

$$A_0 = -NkT \ln [e^{\beta J} + e^{-\beta J}\,] = -NkT \ln [2\cosh(\beta J)\,] \qquad (13.11.11)$$

From this result, the expressions for the internal energy and specific heat of the lattice are given by

$$U_0 = -NJ \tanh(\beta J) \tag{13.11.12}$$

$$C_0 = Nk(\beta J)^2 \operatorname{sech}^2(\beta J) \tag{13.11.13}$$

The variation of the field-free specific heat of lattice with temperature is shown in Fig.13.15.

Finally the magnetization can be obtained from (13.11.10)

$$\langle M(B,T)\rangle = (\partial A/\partial B)_T = N\mu\,(\sinh(\beta\mu B)/[e^{-4\beta J} + \sinh^2(\beta\mu B)]^{1/2}) \tag{13.11.14}$$

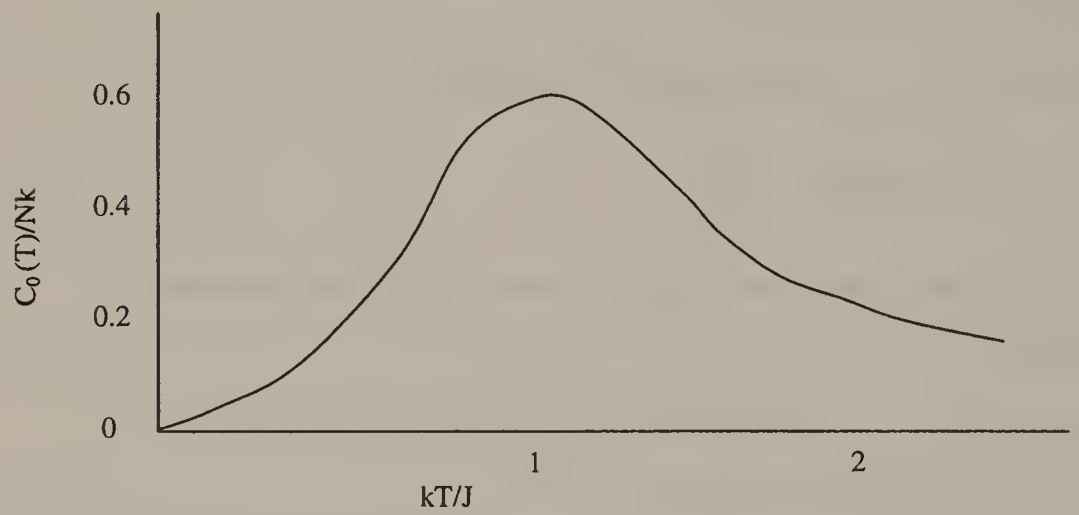


Fig.13.15. The field- free specific heat C_o/Nk of an Ising chain as a function of temperature kT/J.

We see that for B = 0, there is no spontaneous magnetization at any non-zero temperature, i.e. for all T > 0,

$$\langle M(0,T)\rangle/N = 0 \tag{13.11.15}$$

Therefore the one-dimensional Ising model never exhibits ferromagnetism.

13.12. Order Parameter

All phase transition problems can be described in precisely similar terms by introducing the concept of an order parameter. We define the order parameter Q in such a way that it takes nonzero value in the order phase and zero value in the disordered phase. The nonzero value of the order parameter corresponds to the unsymetric phase, and zero value to the symmetric phase. Thus the order parameter takes different values in the co-existing phases and hence, changes discontinuously in the course of a phase transition. The magnitude of the change describes the amount of difference between the co-existing phases.

For example, we consider the liquid-gas phase transition. In this phase transition the order parameter is the number density difference $(\rho_l - \rho_g)$. At low temperature, the density difference $\rho_l - \rho_g$ is large. It decreases with increase in temperature and tends to zero at the critical temperature T_c. At

$T > T_c$, the phase transition disappears. A ferromagnet behaves precisely in an analogous fashion. The order parameter in this case is the spontaneous magnetisation M_0, which decreases when temperature increases, and tends to zero at the critical or Curie temperature T_c. At $T > T_c$, the spontaneous magnetisation remains zero and the phase transition disappears.

When the order parameter changes discontinuously at the transition, the transition is first order. When there is no such discontinuity, the transition is second order. In the second-order transition, the order parameter has a continuous change. The absence of any discontinuous change of state at a phase-transition point of the second order has the result that the thermodynamic functions of the state of the system (e.g. volume, energy, enthalpy, etc.) vary continuously at the transition point.

13.13. Landau Theory

In this section we discuss the thermodynamic behaviour of the system for a deviation from the symmetrical state. During this deviation, the order parameter changes from zero to a given value Q. For this, we start with the free energy A, which is assumed to be a function of T and Q. However, the variable Q must itself be determined from the condition of thermal equilibrium. In thermal equilibrium A(T,Q) is minimum for a given T. In a phase transition of the second order, where the change of state is continuous, the order parameter Q takes an arbitrarily small value near the transition point. We consider the change in the vicinity of the transition point and expand A (T,Q) in powers of Q

$$A(T,Q) = A_0(T) + \alpha Q + \beta Q^2 + \gamma Q^3 + \delta Q^4 + \ldots \qquad (13.13.1)$$

where the coefficients α, β, γ, δ, ... are functions of T.

Since a transition point of the second order must be a singularity of the free energy, such an expansion cannot contain higher order terms. The nature of the singularity of the free energy can be explained with the help of a theory proposed by Landau (1937). This theory is based on the assumption that the presence of the singularity does not affect the terms appearing in the expansion (13.13.1).

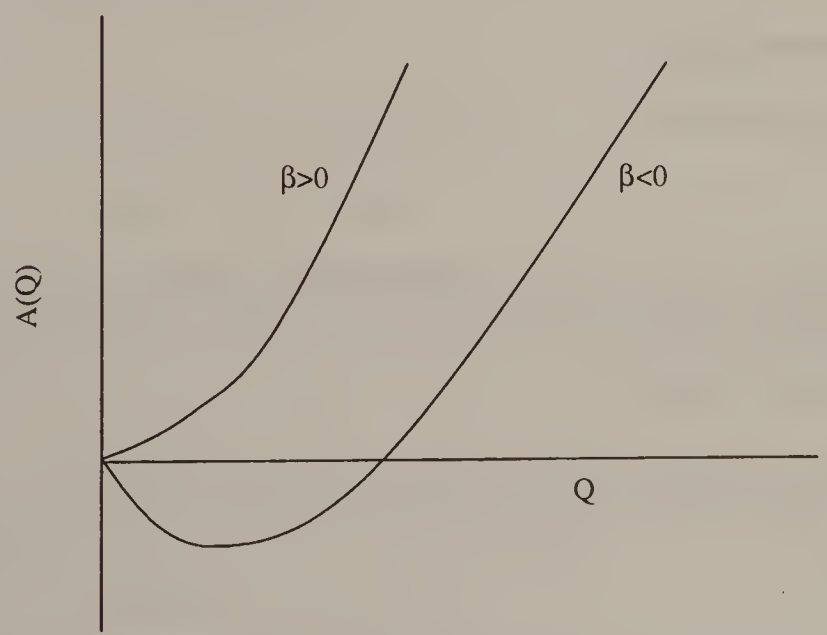


Fig.13.16. The function A(Q) for $\beta < 0$ and $\beta > 0$ is shown as a function of Q

We assume that when the states with $Q = 0$ and $Q \neq 0$ are of different symmetry, the first order term of (13.13.1) is zero, i.e.

$$\alpha = 0$$

Let us now consider the other expansion coefficients β, γ, δ ... appearing in (13.13.1). In the symmetric phase, $Q = 0$, which corresponds to a minimum of A. For this, it is necessary that $\beta > 0$. On the other hand, in the unsymmetric phase, $Q \neq 0$ will correspond to the stable state (i.e. to the minimum of A). This is possible only when $\beta < 0$. The function A(Q) for $\beta < 0$ and $\beta > 0$ is shown in Fig.13.16. Since $\beta < 0$ on one side of the transition point, and $\beta > 0$ on the other side, it must be zero at the transition point, i.e.

$$\beta_c(T) \equiv \beta(T_c) = 0 \qquad (13.13.2)$$

When the transition point itself is a stable state, A(Q) is a minimum at $Q = 0$, and then it is necessary that at the transition point

$$\gamma_c(T) = 0$$

$$\delta_c(T) > 0 \qquad (13.13.3)$$

The coefficient δ, which is positive at the transition point, is also positive in the vicinity of that point.

We consider the case, when $\gamma(T) = 0$ owing to the symmetry of the crystal; then (13.13.1) takes the form

$$A(T,Q) = A_c(T) + \beta(T)Q^2 + \delta(T)Q^4 + ... \qquad (13.13.4)$$

where

$$\beta > 0 \quad \text{(the symmetrical phase)}$$

$$< 0 \quad \text{(the unsymmetrical phase)}$$

and

$$\delta > 0$$

In this case, the phase transition between the states $Q = 0$ and $Q \neq 0$ is second order. Then, we obtain the equation of state in the form

$$\xi = (\partial A/\partial Q) = 2\beta(T)Q + 4\delta(T)Q^3 + ... \qquad (13.13.5)$$

We now assume that we can expand the coefficients $\beta(T)$ and $\delta(T)$ in powers of $\Delta T \equiv T - T_c$. Thus we write

$$\beta(T) = \beta_0 + \beta_1\Delta T + ... \qquad (13.13.6a)$$

$$\delta(T) = \delta_0 + \delta_1\Delta T + ... \qquad (13.13.6b)$$

where $\beta_0 = \beta(T_c)$, $\beta_1 = [\partial\beta/\partial T]_{T=T_c}$

$$\delta_0 = \delta(T_c),\ \delta_1 = [\partial\delta/\partial T]_{T=T_c}$$

We define the transition point by the equation

$$\beta(T) = 0$$

i.e.

$$\beta_0 = \beta(T_c) = 0$$

Let us consider a phase transition. Near the transition point, represented by the transition temperature T_c, we can write

$$\beta(T) = \beta_1 \Delta T = \beta_1 (T - T_c) \qquad (13.13.7)$$

$$\delta(T) \quad \delta_0 \qquad (13.13.7)$$

where β_1 is a constant.
In the unsymmetrical phase, A(Q) is a minimum as a function of Q, so that

$$\partial A/\partial Q = 0$$

and from (13.11.5), we get

$$2\beta Q + 4\delta Q^3 = 0$$

or

$$Q(\beta + 2\delta Q^2) = 0 \qquad (13.13.8)$$

Hence we obtain two values for Q

$$Q = 0 \qquad (13.13.9a)$$

which corresponds to the symmetrical phase and

$$Q^2 = -\beta/2\delta = \beta_i (T_c - T)/2\delta_0 \qquad (13.13.9b)$$

which corresponds to the unsymmetrical phase.

Equation (13.13.4) can be used to calculate the thermodynamic properties of the system near the phase transition point. Neglecting the higher powers of Q, (13.13.4) takes the form

$$A(T, Q) = A_0(T) + \beta Q^2 \qquad (13.13.10)$$

where Q = 0 for the symmetrical phase and $Q = \beta_1 (T_c - T)/2\delta_0$ for the unsymmetrical phase. Then the entropy of the system near the transition point is given by

$$S = -(\partial A/\partial T) = S_0 - (\partial\beta/\partial T)\, Q^2 \qquad (13.13.11)$$

where $S_0 = -\partial A_0/\partial T$ and $\partial Q/\partial T = 0$ because $\partial A/\partial Q = 0$. From (1.13.11) we get for the symmetrical phase

$$S = S_0 \tag{13.13.12a}$$

and for the unsymmetric phase

$$S = S_0 + (\beta_1^2/2\delta_0)\,(T - T_c) \tag{13.13.12b}$$

The internal energy is

$$U = U_0 + (\beta - T(\partial\beta/\partial T))Q^2 \tag{13.13.13}$$

where $U_0 = A_0 + TS_0$, which gives for the state $Q = 0$

$$U = U_0 \tag{13.13.14a}$$

and for the state $Q \neq 0$

$$U = U_0 + (\beta_1^2/2\delta_0)T_c\,(T - T_c) \tag{13.13.14b}$$

At the transition point T_c, $S = S_0$ and $U = U_o$, and thus the entropy and the energy are continuous. Using the relation

$$C_P = T(\partial S/\partial T)_P$$

one can determine the specific heat of two phases near the transition point. For the symmetrical phase, we have

$$C_P = C_{P0} \tag{13.13.15a}$$

and for the unsymmetrical phase

$$C_P = C_{P0} + (\beta_1^2/2\delta_0)T_c \tag{13.13.15b}$$

At the transition point (i.e. at T_c), $C_P > C_{P0}$, since $\delta>0$, and the specific heat is discontinuous at the phase point of the second kind.

Not only C_P but other thermodynamic quantities, such as the thermal expansion coefficient and the compressibility can be shown to be discontinuous at the transition point of the second kind. Thus Landau theory leads us to the conclusion that the first derivatives of quantities such as entropy and volume must be discontinuous at the transition point of the second kind.

13.14. Correlation of Fluctuations and Correlation Length

We consider a homogeneous isotropic system (gas or liquid) containing N identical particles enclosed in a volume V. The particles are uniformly distributed in space and particle number density $n(\mathbf{r})$ is a function of the position vector $\mathbf{r}$. The fluctuation of the number density is $\Delta n = n(\mathbf{r}) - \langle n(\mathbf{r})\rangle$, where $\langle n(\mathbf{r})\rangle$ is the mean particle density.

Let the system contain a number of small subsystems. When two subsystems are non-interacting, their fluctuation can be consider as statistically independent or uncorrelated. However, the fluctuations

of neighbouring subsystems are correlated because of interactions between the particles.. In particular, the fluctuations of the number of particles of two infinitesimal volume elements will be highly correlated.

Let $n(\mathbf{r}_1)d\mathbf{r}_1$ be the number of particles in a volume element $d\mathbf{r}_1$ at a position $\mathbf{r}_1$ and $n(\mathbf{r}_2)d\mathbf{r}_2$ be the number of particles in the volume element dr_2 at r_2. Then,

$$\int(n(\mathbf{r}_1) - \langle n(\mathbf{r}_1)\rangle)d\mathbf{r}_1 = \int(n(\mathbf{r}_2) - \langle n(\mathbf{r}_2)\rangle)d\mathbf{r}_2 = N - \langle N\rangle \equiv \Delta N \tag{13.14.1}$$

where N is the total number of particles in the volume V and ΔN is the fluctuation of N from the mean value $\langle N\rangle$. Let us now consider the mean value

$$\int(n(\mathbf{r}_1) - \langle n(\mathbf{r}_1)\rangle)(n(\mathbf{r}_2) - \langle n(\mathbf{r}_2)\rangle)\, d\mathbf{r}_1 d\mathbf{r}_2 = \langle(N - \langle N\rangle)^2\rangle = \langle N^2\rangle - \langle N\rangle^2 \equiv \langle(\Delta N)^2\rangle \tag{13.14.2}$$

In case of homogeneous fluid, $\langle n(\mathbf{r}_1)\rangle = \langle n(\mathbf{r}_2)\rangle = \ldots = \rho$, where $\rho = \langle N\rangle/V$ is the number density.

The mean square fluctuation of the number density can be expressed in terms of the correlation function. As discussed in Sec.11.2, the mean square fluctuation of N is expressed in terms of the integral of the correlation function [viz.Eq.(11.2.31)] as

$$\langle N\rangle^2 - \langle N\rangle^2 = \langle N\rangle\,[1 + \rho \int h(r)\, d\mathbf{r}] \tag{13.14.3}$$

The isothermal compresibility is given by the relation

$$kT\,\rho K_T = kT(\partial\rho/\partial P)_T = 1 + \rho \int h(r)\, d\mathbf{r} \tag{13.14.4}$$

For an ordinary ideal gas, when $P = \rho kT$, (13.14.4) gives

$$\rho \int h(r)\, d\mathbf{r} = 0$$

as it should be, because there is no correlation between the positions of non-interacting particles.

From (13.14.2) and (10.14.3), we get

$$\int(n(\mathbf{r}_1) - \langle n(\mathbf{r}_1)\rangle)(n(\mathbf{r}_2) - \langle n(\mathbf{r}_2)\rangle)\, d\mathbf{r}_1 d\mathbf{r}_2 = \int \langle n(\mathbf{r}_1)\rangle\, \delta(\mathbf{r}_1 - \mathbf{r}_2)\, d\mathbf{r}_1 d\mathbf{r}_2 + \int\langle n(\mathbf{r}_1)\rangle\langle n(\mathbf{r}_2)\rangle\, h(r_{12})\, d\mathbf{r}_1 d\mathbf{r}_2$$

or

$$\langle(n(\mathbf{r}_1) - \langle n(\mathbf{r}_1)\rangle)\,(n(\mathbf{r}_2) - \langle n(\mathbf{r}_2)\rangle)\rangle = \langle n(\mathbf{r}_1)\rangle\, \delta(\mathbf{r}_1 - \mathbf{r}_2) + \langle n(\mathbf{r}_1)\rangle\langle n(\mathbf{r}_2)\rangle\, h(r_{12}) \tag{13.14.5}$$

Multiplying both sides of (13.14.5) by $\exp[-i\mathbf{k}.(\mathbf{r}_1-\mathbf{r}_2)]=\exp[-i\mathbf{k}.\mathbf{r}]$ and integrating over $\mathbf{r}_1$ and $\mathbf{r}_2$, we get

$$\langle(\Delta\hat{n}(\mathbf{k}))^2\rangle \equiv \langle(\hat{n}(\mathbf{k}) - \langle\hat{n}(\mathbf{k})\rangle)^2\rangle = \rho V(1 + \rho \int h(r) \exp[-i\mathbf{k}.\mathbf{r}]d\mathbf{r}) = \rho V S(\mathbf{k}) \tag{13.14.6}$$

where

$$\Delta\hat{n}(\mathbf{k}) \equiv \hat{n}(\mathbf{k}) - \langle\hat{n}(\mathbf{k})\rangle = \int (n(\mathbf{r}_1) - \langle n(\mathbf{r}_1)\rangle) \exp[-i\mathbf{k}.\mathbf{r}_1]d\mathbf{r}_1 \tag{13.14.7}$$

$$S(\mathbf{k}) = 1 + \rho \int h(r) \exp[-i\mathbf{k}.\mathbf{r}]d\mathbf{r} = 1 + \rho \hat{h}(\mathbf{k}) \quad (13.14.8)$$

$\hat{\Delta n}(\mathbf{k})$ is the Fourier transform of $n(\mathbf{r}_1) - \langle n(\mathbf{r}_2)\rangle$ and $S(\mathbf{k})$ is the structure factor. Equation (13.14.6) gives the mean square of the Fourier transform of the particle density $n(\mathbf{r}_1)$ in terms of the structure factor.

Taking the Fourier transform of the Ornstein-Zernike Eq.(9.7.10), we obtain a relation between $\hat{h}(k)$ and $\hat{c}(k)$

$$\hat{h}(k) = \hat{c}(k) / (1 - \rho \hat{c}(k)) \quad (13.14.9)$$

and expression for the structure factor S(k)

$$S(k) = 1 + \rho h(k) = [1 - \rho c(k)]^{-1} \quad (13.14.10)$$

where $\hat{c}(k)$ is given by

$$\rho\hat{c}(k) = \rho \int c(r) \exp[-i\mathbf{k}.\mathbf{r}]\, d\mathbf{r} = 4\pi\rho \int c(r) (\sin kr/kr)\, r^2\, dr \quad (13.14.11)$$

From (11.3.9) and (13.14.10) we immediately deduce that

$$\rho\hat{c}(0) = 1 - (1/S(0)) = 1 - (K_T^0/K_T) \quad (13.14.12)$$

since

$$K_T \to \infty \text{ as } T \to T_c,$$

Equation (11.3.9) shows that $S(0) \to \infty$ as $T \to T_c$, i.e. in the vicinity of the critical point, S(k) has a sharp peak at the origin. However, $\hat{c}(0)$ is always finite even at the critical point according to (13.14.12), so that c(r) is a short-ranged function even in the critical region. Thus for large r, $c(r) \to 0$. On the other hand h(r) is long ranged.

Now we consider the behaviour of S(k) in the vicinity of the critical point. Ornstein and Zernike (1918) have calculated the form of S(k) for low k. They assumed that c(k) can be expanded in a Taylor series about k = 0. Thus we can write

$$\rho\hat{c}(k) = 4\pi\rho \int c(r) (\sin kr/kr)\, r^2\, dr = c_0(\rho, T) + c_2(\rho, T)k^2 + 0(k^4) \quad (13.14.13)$$

where

$$c_0(\rho, T) = 4\pi\rho \int c(r)\, r^2\, dr \equiv \rho\hat{c}(0) \quad (13.14.14)$$

$$c_2(\rho, T) = -(2\pi\rho/3) \int c(r)\, r^4\, dr = -R^2 \quad (13.14.15)$$

where R is sometimes referred to as the Debye persistence length.

From (13.14.10) and (13.14.13), it follows that

$$S(k) = 1 + \rho\hat{h}(k) \approx R^{-2}/(K^2 + k^2) \quad (13.14.16)$$

where

$$K^2 = (1 - c_0)R^{-2} = (K_T^0/K_T)R^{-2} \quad (13.14.17)$$

On taking the inverse Fourier transform of (13.14.16), we obtain the asymptotic form of the correlation function h(r)

$$\rho h(r) \quad (1/(2\pi)^3) \int \exp(i\mathbf{k}.\mathbf{r})\, [R^{-2}/(K^2 + k^2)]\, d\mathbf{k}$$

$$(R^{-2}/2\pi^2 r) \int_0^\infty (k \sin kr/(K^2 + k^2))\, dk \qquad (1/4\pi R^2)\, (\exp[-Kr]/r)$$

or

$$h(r) = (1/4\pi\rho R^2)\, (\exp[-Kr]/r) \tag{13.14.18}$$

This equation leads us to an important characteristic of the critical behaviour of the correlation function through a correlation length ξ, defined by

$$\xi = K^{-1} = R\, (K_T/K_T^0)^{1/2} \tag{13.14.19}$$

Since

$$K_T \propto (T - T_c)^{\gamma}$$

the correlation length ξ can be written as

$$\xi \propto (T - T_c)^{-\nu} \tag{13.14.20}$$

where $\nu = \gamma/2$. Thus ξ becomes infinite as $T \to T_c$.

In the limit $\xi \to \infty$, (13.14.18) reduces to

$$h(r) \sim \text{const}/r \tag{13.14.21a}$$

and

$$S(k) \sim \text{const.}/k^2 \tag{13.14.21b}$$

When $1/S(k)$ is plotted as a function of k^2, a straight line is obtained. However, the experimental curves are not strictly linear, but are bend slightly downwards in the limit $k^2 \to 0$. This fact is taken into consideration by introducing an additional critical exponent η. Thus we get at $T = T_c$

$$h(r) \sim \text{const}/r^{1+\eta} \tag{13.14.22a}$$

and

$$S(k) \sim \text{const.}/k^{2-\eta} \tag{13.14.22b}$$

Experimental evidence suggests that η is a small and positive number ($\eta \sim 0.1$).

13.15. Scaling Hypothesis

The van der Waals theory fails to predict quantitatively, the critical behaviour of a system. In recent years, a considerable theoretical progress has been made to provide a better understanding of critical phenomena. The scaling laws proposed by Widom (1965) and Kadanoff (1966) have been extensively used to study the thermodynamic behaviour of a system in the vicinity of the transition point.

The scaling laws are developed in terms of the equation of states for $\mu(\rho, T)$. At the critical point, the chemical potential μ satisfies the conditions,

$$(\partial\mu/\partial\rho)_T = 0\,, \qquad (\partial^2\mu/\partial\rho^2)_T = 0 \tag{13.15.1}$$

To formulate the scaling property of the classical equation, we introduce dimensionless quantities defined as

$$\Delta T^* = (T - T_c)/T_c$$

$$\Delta\rho^* = (\rho - \rho_c)/\rho_c \qquad (13.15.2)$$

$$\Delta\mu^* = [\mu(\rho,T) - \mu(\rho_c,T)]\,\rho_c/P_c$$

where $\mu(\rho_c,T)$ is the chemical potential on the critical isochore at temperature T.
The Taylor expansion of μ^* to first order in ΔT^* can be written in the form

$$\mu^* = \mu_c^* + \mu_{01}\,\Delta T^* + \mu_{11}\,\Delta\rho^*\Delta T^* + \mu_{03}\,(\Delta\rho^*)^3 \qquad (13.15.3)$$

where

$$\mu_{ij} = \partial^{(i+j)}\mu^*/\,\Delta T^{*i}\,\Delta\rho^{*j}$$

It is convenient to define

$$\Delta\mu^* = \mu^*(\rho, T) - \mu^*(\rho_c, T) = \mu^* - \mu_c^* - \mu_{01}\,\Delta T^* \qquad (13.15.4)$$

Then,

$$\Delta\mu^* = \mu_{03}\,(\Delta\rho^*)^3 + \mu_{11}\,\Delta\rho^*\Delta T^* = \mu_{03}\,(\Delta\rho^*)^3\,[1 + (\mu_{11}\,\Delta T^*/\mu_{03}\,(\Delta\rho^*)^2] \qquad (13.15.5)$$

Equation (13.15.5) can be used to obtain the values of critical exponents. For example, $\Delta\mu^* = 0$ along the co-existence curve. Thus (13.15.5) gives

$$\Delta\rho^* = \pm\,(\mu_{11}/\mu_{03})^{1/2}\,\Delta T^{*1/2} = \pm\,B^*\,|\Delta T^*|^{\beta} \qquad (13.15.6)$$

where $\beta = ½$ and $B^* = (\mu_{11}/\mu_{03})^{\beta}$. Similarly along the isotherm, $\Delta T^* = 0$, and hence we get

$$\Delta\mu^* = \mu_{03}\,(\Delta\rho^*)^3 = D^*\,\Delta\rho^*\,|\Delta\rho^*|^{\delta-1} \qquad (13.15.7)$$

where $\delta = 3$ and $D^* = \mu_{03}$.

In terms of these critical exponents, (13.15.5) can be written as

$$\Delta\mu^* = D^*\,(\Delta\rho^*)^{\delta}\,[1 + B^{*1/\beta}\,(\Delta T^*/(\Delta\rho^*)^{1/\beta}] \qquad (13.15.8)$$

We now introduce a new thermodynamic variable x, defined as

$$x = \Delta T^*/(\Delta\rho^*)^{1/\beta} \qquad (13.15.9)$$

which is known as the scaling parameter. Then (13.15.8) takes the form

$$\Delta\mu^* = \Delta\rho^*\,|\Delta\rho^*|^{\delta-1}\,D^*[1 + x/x_0] \qquad (13.15.10)$$

where $x_0 = B^{*1/\beta}$. If $\Delta\mu$ is 'scaled' by $(\Delta\rho^*)^\delta$ then

$$\Delta\mu^*/(\Delta\rho^*)^\delta = D^*[1 + x/x_0] = h(x) \qquad (13.15.11)$$

where

$$h(x) = D^*[1 + x/x_0] = \mu_{03}[1 + x/x_0] \qquad (13.15.12)$$

Equation (13.15.11) is a function of only one independent scaling parameter.

Since $\Delta\mu^*$ is defined by (13.15.4), the scaled equation (13.15.11) is valid in one-phase region, both above and below T_c to first order in ΔT^*.

The scaling hypothesis does not yield the values of β and δ; it simply establishes a relation between them. Other critical exponents can be obtained in terms of them. Thus the scaling hypothesis does not allow us to calculate the critical exponents from first principles. This is possible by the renormalisation group theory proposed by Wilson (1971). However, this is not included in this book.

13.16. Universality of Critical Behaviour

The theoretical studies of various systems indicate a remarkable regularity in the values of α, β and γ. This has led to the formulation of the hypothesis of universality. According to this hypothesis, all phase transition problems can be divided into a number of different classes, depending on the symmetry of the order of state and the dimensionality. The systems belonging to each class have identical critical behaviour. Thus the universality hypothesis implies that systems belonging to the same universality class will asymptotically obey the same scaled equation of states. The critical exponents and the function h(x) will be the same for all these systems. However, the parameter D^* and x_0 will not be the same.

13.17. The Law of Corresponding States

When the pressure, volume and temperature are measured in the units of the critical pressure P_c, critical volume V_c and critical temperature T_c, respectively, i.e.

$$P_r = P/P_c, \quad V_r = V/V_c \text{ and } T_r = T/T_c,$$

then the van der Waal equation of state (Eq.(9.1.20b) reduces to the dimensionless form

$$(P_r + (3/V_r))(V_r - (1/3)) = (8/3)T_r \qquad (13.17.1)$$

This equation does not contain any constant which is characteristic of a gas. Therefore it is a universal equation valid for all substances.

Eq.(13.17.1) is called the 'reduced equation of state' of van der Waal. This equation states that "if any two of the quantities P_r, V_r and T_r are the same for any two substances, then the third quantity is also same for these systems". This is called the law of corresponding states'. The law of corresponding states can be used to determine unknown isotherms of gases if their critical constants are known.

The law of corresponding states is not restricted to the van der Waals equation only. Any equation of state may predict the existence of corresponding states, provided the equation contains three constants (such as a, b and R).

The reduced equation of state may be expressed in terms of other variables instead of the critical constants.

Let us consider gaseous systems whose molecules interact through a pair of potential defined by

$$u(r) = \epsilon\, f(r/\sigma) \tag{13.17.2}$$

which depends on two parameters σ and ϵ. We introduce new reduced variables defined as

$$P^* = P\sigma^3/\epsilon \;; \quad V^* = V/\sigma^3 \;; \quad T^* = kT/\epsilon \tag{13.17.3}$$

They are also dimensionless quantities like P_r, V_r and T_r. Taking these reduced variable, the reduced equation of state may be written in another form

$$P^* = P^*(V^*,T^*) \tag{13.17.4}$$

This is due to deBoer and Michels. In terms of P*, V* and T*, the reduced van der Waals equation of state is written as

$$(P^* - (a^*/V^{*2}))\,(V^* - b^*) = NT^* \tag{13.17.5}$$

where

$$a^* = a/\epsilon\sigma^3 \;; \quad b^* = v/\sigma^3 \tag{13.17.6}$$

deBoer has generalised the law of corresponding states for quantum fluids. The deviation from the classical law due to the quantum effects depends on the dimensionless quantum parameter Λ^* defined by

$$\Lambda^* = h/\sigma\,(m\epsilon)^{1/2}$$

which is a characteristic of the substance considered. Then the new law of corresponding states will be

$$P^* = P^*(V^*, T^*, \Lambda^*) \tag{13.17.7}$$

In the limit $\Lambda^* = 0$, Eq.(13.17.7) reduces to the classical law (13.17.4).

On this basis, various properties of the gaseous systems have been studied. These are found to be in fairly good agreement with experimental results.

Problems

13.1 Derive the Clausius-Clapeyron equation,
$dP/dT = L/T(v_2 - v_1)$

13.2 Show that during the first order phase transition, the Gibbs function is continuous, but the first order derivatives of the Gibbs function change discontinuously.

13.3 Show that during the second order phase transition
$\partial^2 G_1/\partial T^2 \neq \partial^2 G_2/\partial T^2$
and
$\partial^2 G_1/\partial P^2 \neq \partial^2 G_2/\partial P^2$
where G_1 and G_2 are Gibbs functions for phases 1 and 2 respectively.

13.4 Assuming van der Waals equation of state

$(p + (a/v^2))\,(v - b) = RT$
calculate the critical constants in terms of the parameters a and b, and show that
$p_c v_c/RT_c = 8/3$

13.5 Consider a gas which obeys the Dieterici equation of state
$p(v - b) = kT \exp(-1/kTv)$
Calculate the critical constants p_c, v_c and T_c for such a gas in terms of the parameters a and b. Write the equation in a form which shows the law of corresponding states.

13.6 Assuming that a gas obeys the equation of state
$P/\rho kT = ((1+\eta+\eta^2)/(1-\eta)^3) - (a\rho/kT)$
where $\eta = \pi\rho\sigma^3/6$ (σ being the diameter of a molecule), calculate the critical constants P_c, ρ_c and T_c.

13.7 Derive the critical exponents $\gamma = \gamma' = 1$, $\beta = ½$, and $\delta = 3$ from the van der Waals equation of state.

13.8 Explain the spontaneous magnetisation of the Ising model. Discuss the dependence of the order parameter L_0 on temperature T.

13.9 Show that the magnitude of the specific heat discontinuity in the Curie-Weiss theory is 3Nk/2.

13.10 Discuss Landau theory of the order parameter. Explain how this theory shows that the specific heat is discontinuous at the phase point of the second order phase transition.

13.11 Explain the order parameter and correlation length. Show that the correlation length ξ is
$\xi \propto (T - T_c)^{-\nu}$

CHAPTER 14

KINETIC THEORY OF GASES

So far we have considered the properties of system on equilibrium. In this and following chapter, we deal with the situation when the systems are not in equilibrium. The kinetic theory constitutes the basis for the microscopic theory of real gases. The kinetic theory may be based on a detailed knowledge of molecular collisions, which involve the dynamics of interacting particles.

This chapter is devoted to a dilute gas, where only binary collisions are taken into consideration. Collisions of three or more particles become increasingly difficult to treat and can be safely ignored in a dilute gas.

14.1. Boltzmann Transport Equation

Boltzmann developed an integro-differential equation in the distribution function in about 1872, which is the basis for treating the non-equilibrium gases. It was derived on consideration of binary collisions for dilute gases.

The kinetic theory of gases is based on the Boltzmann equation, which specifies the distribution function $f(\mathbf{r}, \mathbf{v}, t)$ so defined that

$$f(\mathbf{r}, \mathbf{v}, t)\, d\mathbf{r}\, d\mathbf{v} \tag{14.1.1}$$

is the number of molecules in a configurational space element $d\mathbf{r}$ at $\mathbf{r}$ and in a velocity space element $d\mathbf{v}$ at $\mathbf{v}$. According to (1.3.4), the probability of finding the number of molecules in the volume element $d\mathbf{r}\, d\mathbf{p}$ of phase space about $(\mathbf{r},\mathbf{p})$ is

$$N^{1}\rho(\mathbf{r},\mathbf{p})\, d\mathbf{r}\, d\mathbf{p} \tag{14.1.2}$$

Using the relation $d\mathbf{p} = m^3 d\mathbf{v}$, where m is the mass of a molecule, the momentum space can be transferred into velocity space. Then comparing (14.1.1) and (14.1.2), we get

$$f(\mathbf{r}, \mathbf{v}, t) = m^3 N \rho(\mathbf{r},\mathbf{p},t) \tag{14.1.3}$$

In order to obtain an explicit expression for $f(\mathbf{r}, \mathbf{v}, t)$, we consider the equation of motion for the distribution function in the six-dimensional space, called the μ-space, spanned by the coordinates $(\mathbf{r},\mathbf{v})$ of a molecule. We consider a volume element $d\mathbf{r}d\mathbf{v}$ in the μ-space. The number of phase points in the volume element changes with time. The phase points move in such a way that a molecule with coordinate $(\mathbf{r},\mathbf{v})$ at the time t, will occupy a point $(\mathbf{r} + \mathbf{v}dt, \mathbf{v} + \mathbf{a}dt)$ at the time $(t + dt)$, where $\mathbf{a} = \mathbf{F}/m$ ($\mathbf{F}$ is the external force acting on a molecule of mass m). In the absence of collisions in the gas, we can write

$$f(\mathbf{r} + \mathbf{v}dt, \mathbf{v} + \mathbf{a}dt, t + dt)\, d\mathbf{r}d\mathbf{v} = f(\mathbf{r}, \mathbf{v}, t)\, d\mathbf{r}\, d\mathbf{v} \tag{14.1.4}$$

However this equality does not hold when there are collisions in the gas. Due to collisions, some phase points are deflected from their paths. Consequently some of the phase points which are initially at a point (**r**,**v**), do not arrive at (**r** + **v**dt, **v** + **a**dt) in the interval dt. Let the number of phase points lost due to collisions in the interval dt be A**dr**dvdt. Similarly, as a result of collisions, some additional molecules arrive at (**r** + **v**dt, **v** + **a**dt) in the interval dt. Let the number of such molecules be B **dr** dv dt. When the effects of collisions are taken into accounts, (14.1.4) becomes

$$f(\mathbf{r} + \mathbf{v}dt, \mathbf{v} + \mathbf{a}dt, t + dt)\, d\mathbf{r}d\mathbf{v} = f(\mathbf{r}, \mathbf{v}, t)\, d\mathbf{r}\, d\mathbf{v} + (B - A)\, d\mathbf{r}\, d\mathbf{v}\, dt \qquad (14.1.5)$$

The function on the left hand side of (14.1.5) may be expanded in a Taylor series about (**r**, **v**, t). Thus

$$f(\mathbf{r} + \mathbf{v}dt, \mathbf{v} + \mathbf{a}dt, t + dt) = f(\mathbf{r}, \mathbf{v}, t) + (\mathbf{v}.\nabla_r f)dt + (\mathbf{a}.\nabla_v f)dt + (\partial f/\partial t)dt \qquad (14.1.6)$$

where ∇_r and ∇_v are the gradient operators with respect to **r** and **v**. Substitution of (14.1.6) in (14.1.5) gives the Boltzmann transport equation

$$(\partial f/\partial t) + \mathbf{v}.\nabla_r f + \mathbf{a}.\nabla_v f = B - A \qquad (14.1.7)$$

where B – A is the change of f, resulting from the collisions. The left hand side of (14.1.7) denotes a net rate of change in the distribution of a flow of phase points. Accordingly, we can define the right hand side of (14.1.7), as

$$(\partial f/\partial t)_{coll} \equiv B - A \qquad (14.1.8)$$

Clearly, (B – A) gives the net gain of molecules per second per unit volume element in the μ-space due to collisions. The term $(\partial f/\partial t)_{coll}$ is called the collisions integral, which indicates the time rate change of f due to collisions.

Let us now derive an explicit expression for the collision integral. For this we assume that the gas is very dilute so that we may consider only binary collisions.

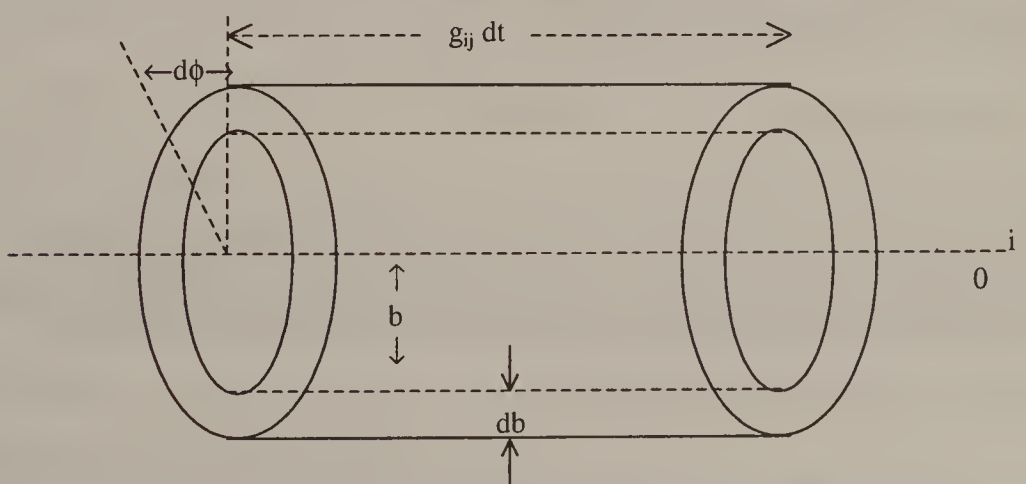


Fig.14.1. Collision of molecules of type j with one molecule of type i fixed at 0. Any molecules of type j located in a cylinder of base bdbdϕ and height g_{ij}dt will undergo a collision with the molecule i during the time interval dt.

We consider a molecule of type i, situated at the position $\mathbf{r}$, and having a velocity $\mathbf{v}_i$. Let us obtain the probability that this molecule will collide with a molecule of type j lying in the impact parameter range b and b+db, in the time interval dt. When the molecule i is assumed to be at rest, the molecule j will move towards it with a relative velocity $(\mathbf{v}_j - \mathbf{v}_i)$ as shown in Fig.14.1. The volume of the cylinder of base bdbdϕ and height g_{ij}dt is

$$dV = g_{ij}\, bdbd\phi dt \tag{14.1.9}$$

where

$$g_{ij} = g_{ji} = |g_{ij}| \equiv |\mathbf{v}_j - \mathbf{v}_i| \tag{14.1.10}$$

Any molecule of type j within this cylinder will undergo a collision with the molecule i during the time interval dt. The probable number of molecules of type j in this cylinder with velocity range $d\mathbf{v}_j$ about $\mathbf{v}_j$ is

$$f_j(\mathbf{r}, \mathbf{v}_j, t)\, g_{ij}\, bdb\, d\phi dt\, d\mathbf{v}_j \tag{14.1.11}$$

The total number of collisions experienced by molecule i with all molecules of type j is given by

$$dt \int\int f_j(\mathbf{r}, \mathbf{v}_j, t)\, g_{ij}\, bdb\, d\phi\, d\mathbf{v}_j \tag{14.1.12}$$

The number of molecules of type i in the volume element $d\mathbf{r}\, d\mathbf{v}$ about $(\mathbf{r}, \mathbf{v}_i)$ is

$$f_i(\mathbf{r}, \mathbf{v}_i, t)\, d\mathbf{r}\, d\mathbf{v}_i \tag{14.1.13}$$

Then the total number of collisions experienced by molecules of type i with all molecules of type j is given by

$$d\mathbf{r}\, d\mathbf{v}_i\, dt \int\int\int f_i(\mathbf{r}, \mathbf{v}_i, t)\, f_j(\mathbf{r}, \mathbf{v}_j, t)\, g_{ij}\, bdb\, d\phi\, d\mathbf{v}_j \tag{14.1.14}$$

The rate A is obtained by summing (14.1.14) over all $\mathbf{v}_j$. Thus

$$A\, d\mathbf{r}\, d\mathbf{v}_i\, dt = d\mathbf{r}\, d\mathbf{v}_i\, dt \sum_j \int\int\int f_i f_j g_{ij}\, bdb\, d\phi\, d\mathbf{v}_j$$

or

$$A = \sum_j \int\int\int f_i f_j g_{ij}\, bdb\, d\phi\, d\mathbf{v}_j \tag{14.1.15}$$

In a similar way we can evaluate B. Let us consider the collisions of the type $\{\mathbf{v}_i, \mathbf{v}_j\} \rightarrow \{\mathbf{v}_i', \mathbf{v}_j'\}$. For every collision there exists the velocities $\mathbf{v}_i'$, $\mathbf{v}_j'$ after collisions in the surrounding. Let f_i' and f_j' be the distribution functions corresponding to the velocities $\mathbf{v}_i'$ and $\mathbf{v}_j'$. These distribution functions can be used to count the probable number of collisions which add particles to the region. Thus we write

$$B\, d\mathbf{r}\, d\mathbf{v}_i\, dt = d\mathbf{r}\, d\mathbf{v}_i\, dt \sum_j \int\int\int f_i' f_j' g_{ij}' b'db' d\phi' d\mathbf{v}_j \tag{14.1.16}$$

For spherically symmetric potentials, the absolute value of the relative velocity and the impact parameter are identical before and after collision, i.e.

$$g_{ij} = g_{ij}'$$

$$b = b'$$

Further, we assume that $dv_i' dv_j' = dv_i\, dv_j$. When these facts are used, we get

$$B\, d\mathbf{r}\, dv_i\, dt = d\mathbf{r}\, dv_i\, dt \sum_j \int\int\int f_i' f_j' g_{ij}\, bdb\, d\phi\, dv_j$$

or

$$B = \sum_j \int\int\int f_i' f_j' g_{ij}\, bdb\, d\phi\, dv_j \qquad (14.1.17)$$

where f_i' and f_j' represent $f_i'(\mathbf{r}, \mathbf{v}_i', t)$ and $f_j'(\mathbf{r}, \mathbf{v}_j', t)$, respectively.

For a one-component gas, A and B become

$$A = \int\int\int f_1 f_2\, gb\, db\, d\phi\, dv_2 \qquad (14.1.18)$$

$$B = \int\int\int f_1' f_2'\, gb\, db\, d\phi\, dv_2 \qquad (14.1.19)$$

Substituting the values of A and B in (14.1.7), we obtain an equation for f.

$$(\partial f_1/\partial t) + \mathbf{v}.\nabla_r f_1 + \mathbf{a}.\nabla_v f_1 = \int\int\int (f_1' f_2' - f_1 f_2)\, gb\, db\, d\phi\, dv_2 \qquad (14.1.20)$$

where

$$f_1 \equiv f(\mathbf{r}, \mathbf{v}_1, t) \qquad f_1' \equiv f(\mathbf{r}, \mathbf{v}_1', t)$$

$$f_2 \equiv f(\mathbf{r}, \mathbf{v}_2, t) \qquad f_2' \equiv f(\mathbf{r}, \mathbf{v}_2', t) \qquad (14.1.21)$$

This is known as the Boltzmann integro- differential equation for the distribution function f. This equation forms the basis for discussing the transport properties of gases.

14.2. Boltzmann's H-Theorem

Let us consider the Boltzmann equation when there is no external force. It is then consistent to assume that the function f is independent of **r**. Hence the distribution function is denoted by $f = f(\mathbf{v},t)$, and the Boltzmann equation [Eq.14.1.20)] reduces to

$$(\partial f_1/\partial t) = \int\int\int (f_1' f_2' - f_1 f_2)\, |\mathbf{v}_2 - \mathbf{v}_1|\, bdb\, d\phi\, dv_2 \qquad (14.2.1)$$

We consider the function of time

$$H(t) = \int f_1(\mathbf{v}_1, t) \ln f_1(\mathbf{v}_1, t)\, dv_1 \qquad (14.2.2)$$

which is known as the Boltzmann function. Defferentiating with respect to time, we obtain,

$$dH/dt = \int (\partial f_1/\partial t)\, [1 + \ln f_1]\, dv_1 \qquad (14.2.3)$$

Substituting (14.2.1) in (14.2.3), we get

$$dH/dt = \int\int\int |\mathbf{v}_2 - \mathbf{v}_1|\, (f_1' f_2' - f_1 f_2)\, (1 + \ln f_1)\, bdbd\phi dv_1 dv_2 \qquad (14.2.4)$$

Interchanging $\mathbf{v}_1$ a $\mathbf{v}_2$ in this integrand, the integral remains invariant. Thus

$$dH/dt = \int\int\int\int |v_1 - v_2| (f_1' f_2' - f_1 f_2) (1 + \ln f_2) \, bdbd\phi dv_1 dv_2 \qquad (14.2.5)$$

Adding (14.2.4) and (14.2.5) together gives

$$dH/dt = (1/2)\int\int\int\int |v_2 - v_1| (f_1' f_2' - f_1 f_2) [2 + \ln(f_1 f_2)] \, bdbd\phi dv_1 dv_2 \qquad (14.2.6)$$

Since for every collision there is an inverse collision with the same impact parameter, this integral remains invariant under the interchange of $\{\mathbf{v}_1, \mathbf{v}_2\}$ and $\{\mathbf{v}_1', \mathbf{v}_2'\}$.
Thus

$$\begin{aligned} dH/dt &= (1/2) \int\int\int\int |v_2' - v_1'| (f_1 f_2 - f_1' f_2') [2 + \ln(f_1' f_2')] \, bdbd\phi dv_1' dv_2' \\ &= (1/2) \int\int\int\int |v_2 - v_1| (f_1 f_2 - f_1' f_2') [2 + \ln(f_1' f_2')] \, bdbd\phi dv_1 dv_2 \end{aligned} \qquad (14.2.7)$$

where we have used the fact that $dv_1' dv_2' = dv_1 dv_2$ and $|v_2' - v_1'| = |v_2 - v_1|$. Adding (14.2.6) and (14.2.7), we obtain,

$$dH/dt = -(1/4) \int\int\int\int |v_2 - v_1| (f_1 f_2 - f_1 f_2) \ln(f_1 f_2 / f_1 f_2) \, bdbd\phi dv_1 dv_2 \qquad (14.2.8)$$

Whatever be the values of $f_1' f_2'$ and $f_1 f_2$, the quantity

$$(f_1' f_2' - f_1 f_2) \ln(f_1' f_2' / f_1 f_2) \geq 0$$

Therefore, it follows from (14.2.8) that

$$dH/dt \leq 0 \qquad (14.2.9)$$

which is the famous Boltzmann H-theorem. In (14.2.9) the equality sign holds for the case of equilibrium while the inequality sign holds for the case of non-equilibrium. According to (14.2.8), it follows that

$$\begin{aligned} dH/dt &= 0 \qquad \text{if} \quad f_1' f_2' = f_1 f_2 \\ dH/dt &< 0 \qquad \text{if} \quad f_1' f_2' \neq f_1 f_2 \end{aligned} \qquad (14.2.10)$$

Stationary solutions are possible only if $dH/dt = 0$.

On the basis of the H theorem, Boltzmann made a bold statement that for a system not in equilibrium, H will decrease until it reaches its equilibrium value.

14.3. Relation between H-Function and Entropy

We may define the Boltzmann H function by

$$H = \int f \ln f \, d\mathbf{r} \, dv \qquad (14.3.1)$$

which satisfies the inequality relation

$$dH/dt \leq 0 \qquad (14.3.2)$$

According to thermodynamics the inequality for the entropy of an isolated nonequilibrium system is

$$dS/dt \geq 0 \tag{14.3.3}$$

These two relations suggest that the H function is related to the entropy S.

According to Eq.(5) of section 4.7.1, the entropy of a system in thermodynamic equilibrium is given by

$$S = -k \sum_i \rho_n \ln \rho_n$$

or

$$S = -k \int \rho(X) \ln \rho(X)\, dX \tag{14.3.4}$$

where X stands for both coordinates and momenta, and $\rho(X)$ is the probability density for the canonical distribution. The single particle distribution function is defined by

$$\rho_1(X_i) = \int \rho(X_1, X_2, \ldots, X_N)\, dX_1, \ldots, dX_{i-1} dX_{i+1}, \ldots, dX_N \tag{14.3.5}$$

For an ideal gas, where the molecules are statistically independent, we have

$$\rho(X) = \prod_{i=1}^{N} \rho(X_i) \tag{14.3.6}$$

Substituting (14.3.6) in (14.3.4), we obtain

$$\begin{aligned} S &= -k \sum_{i=1}^{N} \prod_{i=1}^{N} \int \rho_1(X) \ln \rho_1(X_i)\, dX_i \\ &= -k \sum_{i=1}^{N} \int \rho_1(X_i) \ln \rho_1(X_i)\, dX_i \prod_{j \neq 1} \int \rho_1(X_j)\, dX_j \\ &= -k \sum_{i=1}^{N} \int \rho_1(X_i) \ln \rho_1(X_i)\, dX_i \end{aligned} \tag{14.3.7}$$

since from the normalisation condition

$$\int \rho_1(X_j)\, dX_j = 1 \tag{14.3.8}$$

Since the particles are identical, the contribution of all the terms in the sum of (14.3.7) is same, and we can write

$$S = -Nk \int \rho_1(X_1) \ln \rho_1(X_1)\, dX_1 \tag{14.3.9}$$

Substituting (14.1.3) in (14.3.9), we get

$$S = -k \int f(\mathbf{r}, \mathbf{v}) \ln f(\mathbf{r}, \mathbf{v})\, d\mathbf{r}\, d\mathbf{v} + Nk \ln (m^3 N) \tag{14.3.10}$$

Thus for an ideal gas, the entropy S can be written as

$$S = -kH + S_0 \tag{14.3.11}$$

where

$$S_0 = Nk \ln (m^3N) \tag{14.3.12}$$

is a constant. Thus, apart from an additive constant, the entropy of the nonequilibrium system is defined as $-kH$, where k is the Boltzmann constant. Then the H theorem can be interpreted as a generalized second law of thermodynamics, i.e. entropy increases unless the system is in equilibrium which is the law of increase of entropy.

14.4. Maxwell-Boltzmann Distribution

A system will be in the equilibrium state, when

$$dH/dt = 0$$

According to (14.2.8), this occurs only when

$$f_1' f_2' - f_1 f_2 = 0 \tag{14.4.1}$$

Taking the logarithm of both sides of (14.4.1), we get

$$\ln f_1' + \ln f_2' = \ln f_1 + \ln f_2 \tag{14.4.2}$$

This tells us that ln f is conserved in any collision.
Since only momentum and energy are conserved on collision, we must have

$$\ln f = a + b(mv) + c\,((1/2)mv^2) \tag{14.4.3}$$

which can be re-expressed as

$$\ln f = \ln A - (\beta m/2)\,(v - v_0)^2$$

or

$$f = A \exp [-(\beta m/2)\,(v - v_0)^2] \tag{14.4.4}$$

where A, β and v_0 are constants. We can choose $v_0 = 0$, so that

$$f = A \exp [-\beta mv^2/2] \tag{14.4.5}$$

The constant A and β can be evaluated from the conditions

$$\int f\,dv = N/V = \rho \tag{14.4.6}$$

$$\int ((1/2)mv^2)\, f\,dv = (3/2)NkT \tag{14.4.7}$$

Substituting (14.4.5) in (14.4.6) and (14.4.7), we get

$$A = \rho\,(m\beta/2\pi)^{3/2} \tag{14.4.8}$$

$$\beta = (1/kT) \tag{14.4.9}$$

Substituting these values in (14.4.5), we obtain the equilibrium distribution function for a dilute gas

$$f(v) = \rho\,(m/2\pi kT)^{3/2} \exp\,[-m(v - v_0)^2/2kT] \tag{14.4.10}$$

This is the Maxwell distribution for velocities. In deriving (14.4.10), we have neglected external forces.

Let us now consider the equilibrium distribution for a dilute gas in the presence of an external force field **F**, given by

$$\mathbf{F} = -\nabla_r\, U(r) \tag{14.4.11}$$

In this case the equilibrium distribution function will be

$$f(r,v) = f(v) \exp\,[-U(r)/kT] \tag{14.4.12}$$

where f(v) is given by (14.4.10). This is the Maxwell-Boltzmann distribution, first derived by Boltzmann (1868).

It can be shown that (14.4.12) satisfies the Boltzmann equation. In this case, $\partial f/\partial t = 0$ because (14.4.12) is independent of time, and the Boltzmann equation can be written as

$$(\mathbf{v}.\,\nabla_r + (\mathbf{F}/m).\,\nabla_v)\, f = \exp[-2U(r)/kT] \int\int\int [f_0(v_1')\, f_0(v_2') - f_0(v_1)\, f_0(v_2)]\, gb\, db\, d\phi\, dv_2$$

$$= 0 \tag{14.4.13}$$

We may write (14.4.12) in the form

$$f(\mathbf{r}, \mathbf{v}) = \rho(\mathbf{r})\,(m/2\pi kT)^{3/2} \exp\,(-m(v - v_0)^2/2kT) \tag{14.4.14}$$

where

$$\rho(\mathbf{r}) = \int f(\mathbf{r}, \mathbf{v})\, d\mathbf{v} = \rho \exp\,[-U(r)/kT] \tag{14.4.15}$$

14.5. Validity of the Boltzmann Equation

The Boltzmann equation was derived on the basis of two assumptions: (i) mechanical (assumption of binary collisions), and (ii) statistical (assumptions of mechanical chaos). Shortly after the publication of the Boltzmann H theorem, objections were raised by Loschmidt and Zermelo. These objections were based mainly on mechanical considerations. It has been shown that the Boltzmann H theorem is equivalent to the law of increase of entropy [Eq.(14.3.3)], which shows that the macroscopic processes are irreversible. Thus the H theorem demonstrates the irreversibility of the Boltzmann equation. However, the Boltzmann equation was derived from molecular collisions (law of classical mechanics), which are reversible in time. This is the reversibility paradox first pointed out by Loschmidt. In addition to this paradox, there is also the recurrence paradox, pointed out by Zermelo. Zermelo, using a theorem of Poincare, has shown that a system can exhibit increases as well as decreases in the value of H, which is in contradiction to the H theorem. These two paradoxes being based mainly on mechanical considerations, have nothing to do with statistical physics.

The Boltzmann equation is strictly valid for a dilute gas at a instant of time when the gas is in a state of molecular chaos. Then the only real problem is to understand the precise nature of the molecular chaos, and the condition under which the system can remain in equilibrium.

According to the definition of molecular chaos, if $f(\mathbf{v}, t)$ is the probability density of finding a molecule with velocity $\mathbf{v}$ at time $\mathbf{t}$, then the probability of simultaneously finding a molecule with velocity $\mathbf{v}_1$ and another molecule with velocity $\mathbf{v}_2$ at time t is $f(\mathbf{v}_1, t)\, f(\mathbf{v}_2, t)$. It follows from the above statement that a state of the gas, having a given distribution function, may not satisfy the assumption of molecular chaos.

We can now show that when a gas is in a state of molecular chaos, H is at a local peak. Let us consider a gas without an external force, with an initial condition, which is invariant under time-reversal. The distribution function f(v, t) in this case depends only on the magnitude of the velocity $\mathbf{v}$, and not on its direction. We assume that the gas is in a state of molecular chaos and is non-Maxwellian at time t = 0. Then according to the H theorem

$$dH/dt \leq 0 \qquad \text{at } t = 0^+$$

When we consider another gas with the same initial conditions, and with velocities in the reversed direction, then H is the same for this gas, i.e.

$$dH/dt \leq 0 \qquad \text{at } t = 0^+$$

According to the invariance of the equation of motion under time-reversal, the future of the new gas will be the past of the old gas. Thus for the original gas, we have

$$dH/dt \leq 0 \qquad \text{at } t = 0^+$$

$$dH/dt \geq 0 \qquad \text{at } t = 0^-$$

Thus H is at a local peak. When H is not at a local peak, the gas is not in a state of molecular chaos, and the Boltzmann equation cannot be valid at all time.

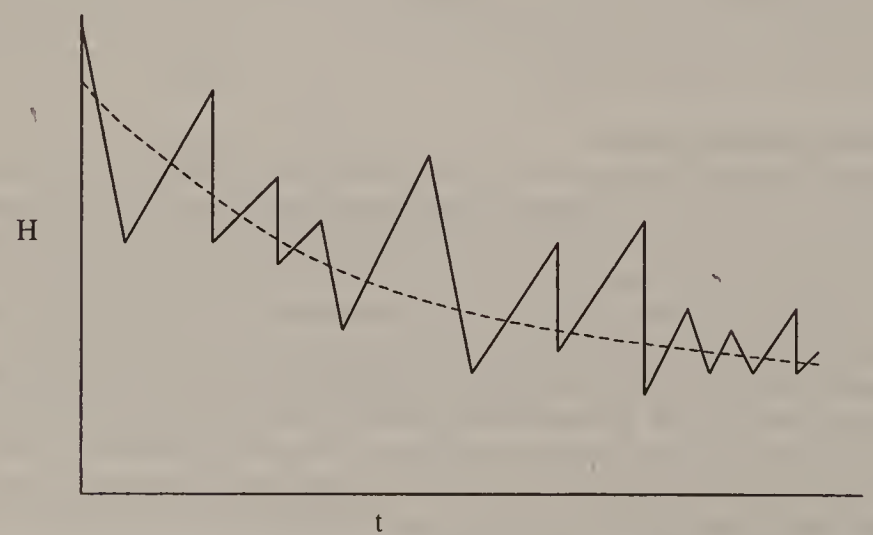


Fig.14.2. H as a function of time t. The solid line represents a real curve and the dashed curve is the value predicted by the solution of the Boltzmann equation. The dotted peaks represent the states of molecular chaos.

It is found that the molecular chaos can be destroyed by collisions. This shows that the Boltzmann equation, once established to be valid, cannot be rigorously valid forever. However, if collisions occur randomly, the distribution function is almost always Maxwell-Boltzmann. In this case the fluctuations from equilibrium due to collisions will have a very short duration of the order of 10^{-11} s. Whenever the distribution function is not strictly Maxwell-Boltzmann. H will be at a local peak. The function is shown in Fig.14.2 as a function of time t, where the solid line is a real curve, the dashed line represents the Boltzmann curve predicted by the Boltzmann transport equation, and the dotted peaks are states of molecular chaos. Hence the Boltzmann equation may be regarded as valid in a statistical sense. It is in this sense that the Boltzmann equation provides a useful description of the approach to equilibrium.

14.6. Mean Free Path

The Boltzmann transport equation (14.1.20) is the fundamental properties of gases and is governed by molecular collisions. To describe any process that depends on molecular collisions, we introduce the concept of mean free path λ, which is the average distance particles travel between two successive collisions.

We consider a gas of identical molecules of diameter σ. If σ is large, collisions are frequent and $\sigma \to 0$, collisions become impossible. A free path is a distance travelled by a molecule between two successive collisions. If $\langle v \rangle$ be the average velocity of a molecule and τ, which is the average time taken in a free path, be the collision time, then the mean free path is given by

$$\lambda = \tau \langle v \rangle \tag{14.6.1}$$

For a gas in equilibrium, the distribution function f(v) is Maxwellian, i.e.

$$f(v) = \rho \, (m/2\pi kT)^{3/2} \exp [-mv^2/2kT] \tag{14.6.2}$$

Then the average velocity $\langle v \rangle$ is

$$\langle v \rangle = \int |v| \, f(v) \, dv = \sqrt{(8kT/\pi m)} \tag{14.6.3}$$

The collision time τ can be estimated from the Boltzmann transport equation. At equilibrium, the number of collisions taking place per second per unit volume at a point **r** in a gas is given by

$$Z\rho = \int\int\int f_1 f_2 \, gb \, db \, d\phi \, dv_1 \, dv_2 \tag{14.6.4}$$

where ρ is the number of molecules per unit volume, and Z is the number of collisions per molecule per second, i.e. the collision frequency. Thus its reciprocal is the collision time τ, i.e.

$$\tau = Z^{-1}$$

Figure 14.3 shows the collision between two identical spherical molecules of diameter σ. The impact parameter b is

$$b = \sigma \sin\psi$$

or

$$b \, db = \sigma^2 \sin\psi \cos\psi \, d\psi$$

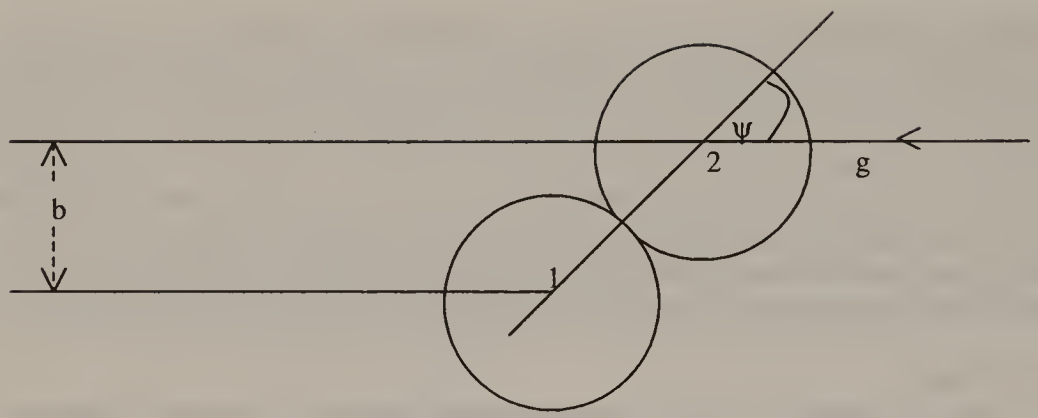


Fig.14.3. Collision between identical hard sphere molecules of diameter σ

(where $0 < \psi < \pi/2$). Integrating over ψ and ϕ, we get

$$Z\rho = \sigma^2 \int\int f_1 f_2 g d\mathbf{v}_1 d\mathbf{v}_2 \int_0^{\pi/2} \sin\psi \cos\psi \, d\psi \int_0^{\pi/2} d\phi$$

$$= \pi\sigma^2 \int\int f_1 f_2 g d\mathbf{v}_1 d\mathbf{v}_2 \qquad (14.6.5)$$

Substituting the Maxewell-Boltzmann distribution (14.6.2) for f_1 and f_2, we get

$$Z\rho = \pi\sigma^2\rho^2 (m/2\pi kT)^3 \int\int d\mathbf{v}_1 d\mathbf{v}_2 \, |\mathbf{v}_2 - \mathbf{v}_1| \exp[-m(v_1^2 + v_2^2)/2kT] \qquad (14.6.6)$$

Let us put

$$\mathbf{V} = (\mathbf{v}_1 + \mathbf{v}_2)/2$$

$$\mathbf{v} = (\mathbf{v}_2 - \mathbf{v}_1)$$

then

$$d\mathbf{v}_1 \, d\mathbf{v}_2 = d\mathbf{V} \, d\mathbf{v}$$

and (14.6.6) can be written as

$$Z = \pi\sigma^2\rho (m/2\pi kT)^3 \int d\mathbf{V} \int d\mathbf{v} \, \mathbf{v} \exp[-(m/2kT)(2V^2 + (1/2)v^2)] \qquad (14.6.7)$$

This can be integrated to give

$$Z = 4\sigma^2\rho (\pi kT/m)^{1/2} = \sqrt{2}\,\pi\sigma^2\rho \langle v \rangle$$

where

$$\langle v \rangle = \sqrt{(8kT/\pi m)}$$

is the average velocity of a Maxwellian gas. Hence the collision time in a dilute gas is

$$\tau = Z^{-1} = (\sqrt{2}\,\pi\sigma^2\rho \langle v \rangle)^{-1} \qquad (14.6.9)$$

and the mean free path is

$$\lambda = (\sqrt{2}\pi\sigma^2\rho)^{-1} \tag{14.6.10}$$

We can express the mean free path in terms of the total scattering cross section $\sigma_o(v)$ for collisions between molecules with velocities $\mathbf{v}_1$ and $\mathbf{v}_2$. We assume that $\sigma_o(v)$ is not sensitive to the energy of the colliding molecules, and may be replaced by a constant of order $\pi\sigma^2$. Thus the mean free path λ and collision time τ can be expressed as

$$\lambda = (\sqrt{2}\sigma_0\rho)^{-1} \tag{14.6.11}$$

$$\tau = (\sqrt{2}\,\sigma_0\rho\,\langle v\rangle)^{-1} \tag{14.6.12}$$

We find that the mean free path is independent of temperature, and is inversely proportional to $\rho\sigma_0$. Equation (14.6.11) and (14.6.12) are good estimates for a dilute gas not far from equilibrium, which is the only case of interest in this chapter. For H_2 gas in intersteller space, the density ρ is ~1 molecule/cm^3. We estimate the mean free path $\lambda \approx 10^{15}$ cm $\approx 10^{-3}$ light-years, where the diameter σ of H_2 is taken to be 10^{-8} cm.

14.7. Transport Properties

The Boltzmann equation can be applied to estimate the transport properties, such as viscosity, thermal conductivity, and mass diffusivity. However, this approach turns out to be mathematically involved. Therefore an approximate approach is often used by the introduction of the mean free path.

Let χ be any transport property associated with a molecule, which varies from layer to layer. Thus the molecules are considered as carriers of the transport property. We considered three unit layers A, O and B situated in a gas, such that AO = OB = λ. Let the transport property of a particle in the plane y_0 be χ_0. Then the transport property of a particle at $y_0 + \lambda\cos\theta$ is $\chi(y_0 + \lambda\cos\theta)$, which can be expressed with the help of Taylor-series expansion as

$$\chi(y_0 + \lambda\cos\theta) = \chi_0 + \lambda\cos\theta\,(d\chi/dy)_{y_0} \tag{14.7.1}$$

where

$$\chi_0 \equiv \chi(y_0)$$

Similarly the value of χ for particle at $y_0 - \lambda\cos\theta$ is

$$\chi(y_0 - \lambda\cos\theta) = \chi_0 - \lambda\cos\theta\,(d\chi/dy)_{y_0} \tag{14.7.2}$$

Let us determine the rate at which molecular properties are transformed across any plane within the gas. We consider a cylinder of height v and base ds such that the volume of the cylinder is $\mathbf{v}.\hat{\mathbf{n}}\,ds$, where $\hat{\mathbf{n}}$ is a unit vector normal to the surface ds. The number of molecules per unit volume in the velocity range $d\mathbf{v}$ is

$$f\,d\mathbf{v}$$

where f is the distribution function. Hence the number of molecules in such a cylinder over the velocity range dv is

$$v.\mathbf{n}f\,d\mathbf{v}\,ds$$

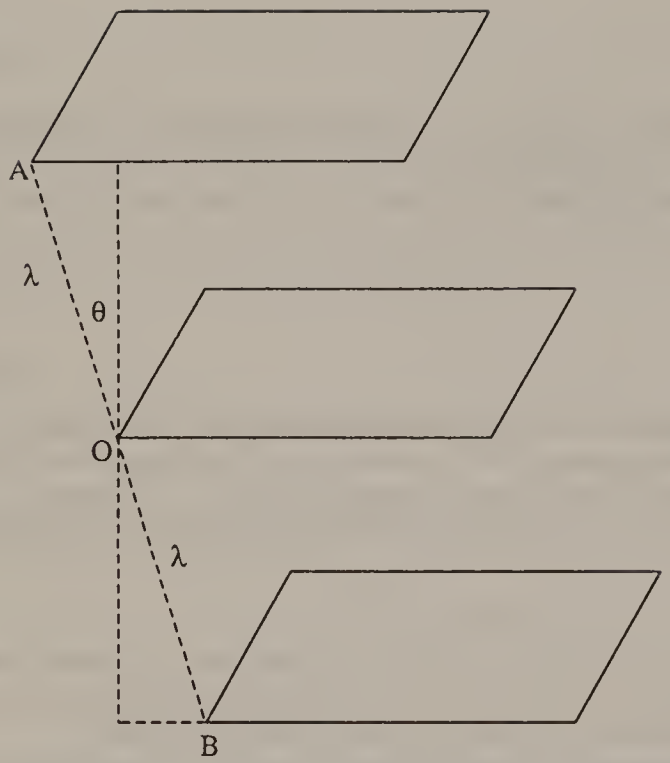


Fig.14.4. Schematic way of calculating transport coefficients. Layers of unit area A and B are at a distance $\lambda \cos\theta$ from the layer at O.

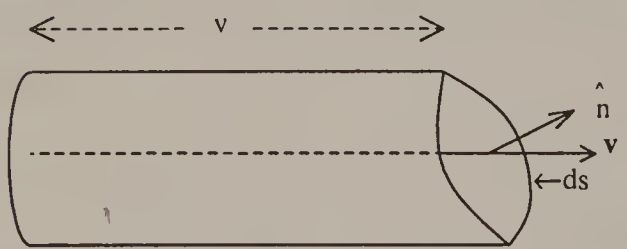


Fig.14.5. The cylinder of height v and base ds. All the molecules with velocity v contained in the cylinder will cross the surface ds per second.

which will cross the surface area ds per second. Hence the net transport of χ across the element area per second is

$$\int_v \chi\,(\mathbf{v}.\hat{\mathbf{n}} f\, d\mathbf{v})\, ds$$

and the net transport of χ per unit area per second (which is flux of χ) is

$$J\chi = \int \chi\, \mathbf{v}.\hat{\mathbf{n}} f\,(v)\, d\mathbf{v} \qquad (14.7.3)$$

Similarly, the net transport of molecules per unit area per second (which is the flux of molecules) is

$$J_{mol} = \int \mathbf{v}.\hat{\mathbf{n}} f(v)\, d\mathbf{v}$$

$$= \int_0^{\infty} f(v)\, v^3 dv \int_0^{\pi/2} \sin\theta \cos\theta\, d\theta \int_0^{2\pi} d\phi$$

$$= \pi \int_0^{\infty} f(v)\, v^3\, dv \qquad (14.7.4)$$

However, the average velocity of a molecule is evaluated as

$$\rho\langle v\rangle = \int v\, f(v)\, d\mathbf{v} = \int_0^{\infty} f(v)\, v^3 dv \int_0^{\pi} \sin\theta\, d\theta \int_0^{2\pi} d\phi = 4\pi \int_0^{\infty} f(v)\, v^3\, dv \qquad (14.7.5)$$

A comparison of (14.7.4) and (14.7.5) gives

$$J_{mol} = (1/4)\, \rho \langle v\rangle \qquad (14.7.6)$$

This is general equation not restricted to Maxwellian gases.

Substituting (14.7.1) in (14.7.3), and integrating θ and ϕ, we get

$$J_\chi^+ = \int_0^{\infty} f(v)\, v^3 dv \int_0^{\pi/2} [\chi_0 + \lambda (d\chi/dy)_{y_0} \cos\theta\,] \cos\theta \sin\theta\, d\theta \int_0^{\pi/2} d\phi$$

$$= \pi[\chi_0 + (2/3)\lambda (d\chi/dy)_{y_0}] \int_0^{\infty} f(v)\, v^3 dv$$

$$= (1/4)\, \rho \langle v\rangle [\chi_0 + (2/3)\lambda (d\chi/dy)_{y_0}] \qquad (14.7.7)$$

Similarly, for the flux of χ leaving the bottom layer B, we get

$$J_\chi^- = (1/4)\, \rho \langle v\rangle [\chi_0 - (2/3)\lambda (d\chi/dy)_{y_0}] \qquad (14.7.8)$$

Then the net flux of χ, $J\chi$ crossing the surface $y = y_0$ from B to A is

$$J_\chi = J_\chi^- - J_\chi^+ = -(1/3)\, \rho \langle v\rangle \lambda (d\chi/dy)_{y_0} \qquad (14.7.9)$$

Viscosity of gases

Let us explain the viscosity of a gas on the basis of the theory of transport properties. The mass of a gas may be assumed to have various layers which are in relative motion due to its viscosity. The coefficient of viscosity η of a gas is defined as a tangential force per unit area per unit velocity gradient, and is given by the relation

$$F = -\eta (du/dy) \qquad (14.7.10)$$

In this case the transport property is momentum, i.e.

$$\chi = mv \equiv mu \tag{14.7.11}$$

Substituting this value in (14.7.9), we get an expression for the momentum flux

$$J_{mom} = -(1/3)\,\rho m \langle v \rangle \lambda\,(du/dy) \tag{14.7.12}$$

The momentum flux or rate of transfer of momentum across an area is equal to the force exerted on the gas to sustain equilibrium. Hence equating (14.7.10) and (14.7.12), we get an expression for the coefficient of viscosity

$$\eta = (1/3)\,\rho m \langle v \rangle \lambda \tag{14.7.13}$$

$$= (1/3)\,\rho_m \langle v \rangle \lambda \tag{14.7.14}$$

where $\rho_m = \rho m$ is the mass density of the gas.

Substituting (14.7.10) in (14.7.13), we get

$$\eta = (1/3\sqrt{2})\,(m\langle v \rangle/\pi\sigma^2) \tag{14.7.15}$$

This shows that η is independent of pressure or density. It only depends on the mass, and the diameter of molecules.

Thermal conductivity

We now explain the thermal conductivity of a gas. In this case the thermal energy varies from layer to layer. Thus in the case of conduction, the molecules are considered as carriers of thermal energy.

Let $\langle \epsilon \rangle$ be the average thermal energy of a molecule. Thus in this case $\chi = \langle \epsilon \rangle$. Substituting this value in (14.7.9), we get an expression for the energy flux

$$J_{energy} = -(1/3)\,\rho \langle v \rangle \lambda\,(d\langle \epsilon \rangle/dy)_{y_0} \tag{14.7.16}$$

If m be the mass of a molecule, then the specific heat at constant volume C_v is given by

$$mC_v = (d\langle \epsilon \rangle/dT)_v = (d\langle \epsilon \rangle/dy)_{y_0}(dy/dT)_{y_0} \tag{14.7.17}$$

or

$$(d\langle \epsilon \rangle/dy) = mC_v\,(dT/dy)_{y_0} \tag{14.7.18}$$

Thus, we obtain

$$J_{energy} = -(1/3)\,\rho m \langle v \rangle \lambda C_v\,(dT/dy)_{y_0} \tag{14.7.19}$$

Let K be the thermal conductivity of the gas, and $(dT/dy)_{y_0}$ be the temperature gradient, then flow of heat per unit area per second will be

$$Q_{y_0} = -K(dT/dy)_{y_0} \tag{14.7.20}$$

Equating (14.7.19) and (14.7.20), we obtain an expression for the thermal conductivity K

$$K = (1/3)\, \rho m \langle v \rangle \lambda C_v = (1/3)\, \rho_m \langle v \rangle \lambda C_v \qquad (14.7.21)$$

With the help of (14.7.14), (14.7.21) can be expressed as

$$K = \eta C_v \qquad (14.7.22)$$

The above relation does not agree with the experimental results. In order to agree with the experimental values, we rewrite

$$K = \beta \eta C_v \qquad (14.7.23)$$

where β is a constant, for monatomic gases, $\beta = 2.5$, and for diatomic gases $\beta = 1.9$.

Substituting (14.6.10) for the mean free path in (14.7.21), we get

$$K = (1/3\sqrt{2})\, (m \langle v \rangle C_v / \pi\sigma^2) \qquad (14.7.24)$$

This shows that like η, K is independent of pressure or density, and varies as $\langle v \rangle / \sigma^2$.

Diffusion

We consider a gas distribution at constant temperature and pressure. The gas is assumed to be made up of different horizontal layers. Imagine a particular horizontal plane O. The molecular concentration varies from layer to layer in the vertical direction (i.e. in the y-axis) but is constant along the horizontal plane in the x-axis. Let ρ be the molecular density, which transports, in this case, the number of molecules crossing unit area of the horizontal plane in unit time (i.e. the mass flux) is

$$J_m = -D\, (d\rho/dy) \qquad (14.7.25)$$

where D is a constant, known as the coefficient of Diffusion.

We can explain the phenomenon of diffusion on the basis of mean free path. We assume that two gases are placed one above the other. Due to their molecular motion, the two gases mix with each other even against gravity. Finally they reach a steady state when the molecular concentrations of the two gases in any horizontal plain attain steady values. However, the molecular concentrations vary in the y direction.

Let ρ_1 and ρ_2 be the numbers of the densities of the two components. Since the number of density ρ of the mixture must be equal to the sum of the components,

$$\rho_1 + \rho_2 = \rho = \text{constant} \qquad (14.7.26)$$

Therefore, the concentration gradients must obey the relation

$$(d\rho_1/dy) + (d\rho_2/dy) = 0$$

or

$$(d\rho_1/dy) = -(d\rho_2/dy) = \alpha \qquad (14.7.27)$$

giving

$$\rho_1 = A_1 + \alpha y \qquad (14.7.28a)$$

$$\rho_2 = A_2 + \alpha y \qquad (14.7.28b)$$

where A_1, A_2 and α are constants.

In this case the number density ρ is the transport property. By analogy with (14.7.9), we can write

$$J_{\rho_1} = -(1/3)\langle v_1\rangle \lambda_1 (d\rho_1/dy) = -(1/3)\,\alpha \langle v_1\rangle \lambda_1 \tag{14.7.29}$$

$$J_{\rho_2} = -(1/3)\langle v_2\rangle \lambda_2 (d\rho_2/dy) = (1/3)\,\alpha \langle v_2\rangle \lambda_2 \tag{14.7.30}$$

The molecular fluxes balance each other i.e.,

$$J_{\rho_1} = -J_{\rho_2} \tag{14.7.31}$$

which gives

$$(1/3)\,\alpha \langle v_1\rangle \lambda_1 = (1/3)\,\alpha \langle v_2\rangle \lambda_2 \tag{14.7.32}$$

It follows from the comparison of (14.7.25) with (14.7.29) and (14.7.30) that

$$D_{12} = (1/3)\langle v_1\rangle \lambda_1 = (1/3)\langle v_2\rangle \lambda_2 = D_{21} \tag{14.7.33}$$

Equation (14.7.33) is accurate only when two components are nearly identical. In this case D_{12} and D_{21} approach a common value D_{11}, known as the coefficient of self-diffusion.

However, in general, $J_1 \neq -J_2$, and there would be a tendency for a net transfer of molecules in an upward direction. This would tend to set up the pressure difference in the gas. But since the pressure must remain constant throughout, this tendency is neutralised by slow mass motion with a mass velocity ω along the y-axis in the direction of decreasing y. Evidently, the velocity ω will be such as establishes the equality of transfer in both directions. Then the actual transfer in both directions will be

$$\Gamma_1 = J_{\rho_1} + \omega\rho_1 \tag{14.7.34}$$

$$\Gamma_2 = J_{\rho_2} + \omega\rho_2 \tag{14.7.35}$$

The fluxes must balance each other, i.e.

$$\Gamma_1 = -\Gamma_2 \tag{14.7.36}$$

which gives

$$\omega = -(J_{\rho_1} + J_{\rho_2})/(\rho_1 + \rho_1) \tag{14.7.37}$$

Thus the true molecular flux in the case of pure diffusion is

$$\Gamma_1 = J_{\rho_1} - ((J_{\rho_1} + J_{\rho_2})/(\rho_1 + \rho_1))\,\rho_1 = ((J_{\rho_1}\rho_2 - J_{\rho_2}\rho_1)/(\rho_1 + \rho_1)) \tag{14.7.38}$$

Substituting (14.7.29) and (14.7.30) along with (14.7.27) in (14.7.38), we can write

$$\Gamma_1 = -(1/3)\,\{(\langle v_1\rangle \lambda_1\rho_2 + \langle v_2\rangle \lambda_2\rho_1)/(\rho_1 + \rho_1)\}\,(d\rho_1/dy) \tag{14.3.39}$$

But from definition

$$\Gamma_1 = - D_{12} (d\rho_1/dy)$$

Therefore, we obtain

$$D_{12} = (1/3) \{(\langle v_1 \rangle \lambda_1 \rho_2 + \langle v_2 \rangle \lambda_2 \rho_1)/(\rho_1 + \rho_1)\}$$

$$= (1/3) [\langle v_1 \rangle \lambda_1 + (\rho_1/(\rho_1 + \rho_1)) (\langle v_2 \rangle \lambda_2 - \langle v_1 \rangle \lambda_1)] \qquad (14.7.40)$$

This is generally known as Mayer's formula for the coefficient of diffusion of one gas into another. D_{12} is often called the coefficient of mutual diffusion. If the molecules of the two gases are approximately identical in size and mass, we can take $\lambda_1 = \lambda_2$ and $\langle v_1 \rangle = \langle V_2 \rangle$. In this case (14.7.40) reduces to (14.7.33). Thus,

$$D_{11} = (1/3) \langle v_1 \rangle \lambda_1 = \eta/\rho_m \qquad (14.7.41)$$

This relation does not agree with the experimental values. In order to improve the agreement with experiments, the equation of Chapman and Enskog yields for the coefficient of self-diffusion,

$$D_{11} = \epsilon \eta/\rho_m \qquad (14.7.42)$$

where for elastic sphere $\epsilon = 1.2$.

14.8. Boltzmann Equation for Quantum Gases

So far we have discussed the classical theory of transport phenomena in gases, where the quantum effects are negligibly small, because the deBroglie wavelength ($\Lambda = h/(2\pi mkT)^{1/2}$) is much smaller than the mean free path. However there are some systems like He, H_2 etc, where the quantum effects are important at low temepratures or at high densities. In this section, we consider the modification to the theory of transport phenomena due to the quantum effects. In this modification it takes into account the diffraction effects and the symmetry (or exchange) effects which are discussed in chapter 10.

If we consider the Boltzmann transport equation for classical particles (Eq.14.1.20), the left hand side of Eq.(14.1.20) is simply the total rate of change in the number of particles and hence is independent of the classical or quantum nature of the particles. On the other hand, the right hand side of Eq.(14.1.20) depends on the collision process going on in the system. So it depends on the nature of the particles. Thus the effect of the quantum nature of the particles will modify the collision terms.

The collision integrals on the right hand side differ from the corresponding classical quantities in two respect (i) gbdb of Eq.(14.1.20) is replaced by $\alpha(g,\chi) \sin\chi \, d\chi$ due to the "diffraction effects", where χ is the angle of deflection after collision of two molecules, and (ii) the factors $(1+\theta f_i)$ is introduced due to the "symmetry effects", where

$$\theta = (h/m)^3 (\delta/G)$$

Here G is the statistical weight of the molecule and

$\delta = 1$ (Bose-Einstein)
$= 0$ (Boltzmann)
$= -1$ (Fermi-Dirac)

Hence the classical development given in Sec.14.1 may be changed to account for the wave-nature of the molecules by replacing gbdb by $\alpha(g, \chi)\sin\chi d\chi$ in Eq.(14.1.20),where $\alpha(g, \chi)$ is known as the scattering probability. Thus, the Boltzmann equation in quantum mechanics is

$$(\partial f_1/\partial t) + \mathbf{v}.\nabla_r f_1 + \mathbf{a}.\nabla_v f_1 = \int\int\int (f_1' f_2' (1+\theta f_1)(1+\theta f_2) - f_1 f_2 (1+\theta f_1')(1+\theta f_2'))\, \alpha(g,\chi) \sin\chi\, d\chi\, d\phi\, dv_2 \tag{14.8.1}$$

Let us consider a one-component gas in volume V, made up of particles obeying Fermi-Dirac statistics. If $Vf(v)dv$ particles have the velocities in the range dv about v, then the probability of collision is reduced in the ratio $[1- f(v)(h/m)^3/G]$. This behaviour is associated with the concept of the apparent repulsion between the particles. For Bose-Einstein particles, the probability collision is reduced like $[1 + f(v)(h/m)^3/G]$, which corresponds to the apparent attraction between the particles. For Boltzmann statistics, $\theta = 0$ and all types of collisions are possible.
When the velocity distribution is maxewellian, the number of particles per unit volume is [see Eq.(14.4.10)]

$$f(v)dv = \rho(m/2\pi kT)^{3/2} \exp[-mv^2/2kT]\, dv \tag{14.8.2}$$

and the largest density exists at $v = 0$ where

$$f\, dv = \rho(m/2\pi kT)^{3/2}\, dv \tag{14.8.3}$$

Under normal conditions,

$$\rho(m/2\pi kT)^{3/2}\, dv \ll G(m/h)^3\, dv \tag{14.8.4}$$

and the occupation of the quantum levels is so dilute tnat no degeneration exists. On the other hand in the limit of high densities or low temperatures

$$\rho(m/2\pi kT)^{3/2}\, dv \gg G(m/h)^3\, dv \tag{14.8.5}$$

In this case the degeneracy according to the Bose-Einstein or Fermi-Dirac statistics plays an important role of measuring deviation from the Maxwell-Boltzmann statistics.

14.8.1 Equilibrium distribution

As in the case of classical particles, we must have collision term of (14.8.1) vanish when f is taken to be the equilibrium distribution. Thus in the equilibrium condition, we have

$$f_1' f_2' (1 \pm f_1(h/m)^3/G)(1 \pm f_2(h/m)^3/G) = f_1 f_2 (1 \pm f_1'(h/m)^3/G)(1 \pm f_2'(h/m)^3/G)$$

or

$$(f_1'/(1 \pm f_1'(h/m)^3/G))(f_2'/(1 \pm f_2'(h/m)^3/G)) = (f_1/(1 \pm f_1(h/m)^3/G))(f_2/(1 \pm f_2(h/m)^3/G)) \tag{14.8.6}$$

where the +ve sign stands for Bose particles and the the –ve for Fermi particles.
Taking the logarithm of both sides, we get

$$\ln[f_1'/(1 \pm f_1'(h/m)^3/G)] + \ln[f_2'/(1 \pm f_2'(h/m)^3/G)] = \ln[f_1/(1 \pm f_1(h/m)^3/G)] + \ln[f_2/(1 \pm f_2(h/m)^3/G)] \tag{14.8.7}$$

This tells us that

$$\ln [f / (1 \pm f (h/m)^3/G)]$$

is conserved in any collision. So it must be a linear function of the collision invariant. Hence

$$\ln [f / (1 \pm f (h/m)^3/G)] = \alpha - \beta\epsilon + \boldsymbol{\gamma}.\mathbf{v}_0$$

where we can choose $\mathbf{v}_0 = 0$ and obtain

$$\ln [f / (1 \pm f (h/m)^3/G)] = \alpha - (1/2)\,\beta m v^2 \qquad (14.8.8)$$

which can be solved to give

$$f = G(m/h)^3/[A \exp(mv^2/2) \pm 1] \qquad (14.8.9)$$

where the –ve sign stands for the Bose- particles and the +ve for the Fermi particles. Here A is a constant related to the number density and $\beta = 1/kT$.

Fermi particles

We now consider the degeneracy of the Fermi particles. We consider two cases separately.

(i) when A is large

In this case, we have from (14.8.9)

$$\rho = 2\pi \int_0^\infty f(v)\, v^2\, dv$$

$$= G(m/h)^3\, 2\pi \int_0^\infty [(1/A)\, e^{-mv^2/2kT} - (1/A^2)\, e^{-2mv^2/2kT} - (1/A^3)\, e^{-3mv^2/2kT} - \ldots]\, v^2\, dv$$

$$= G(m/h)^3\, (2\pi mkT/m)^{3/2}\, [(1/A) - (1/2^{3/2}A^2) + (1/3^{3/2}A^3) - \ldots] \qquad (14.8.10)$$

Reversing the series, we obtain the value of 1/A as

$$1/A = (\rho h^3/G(2\pi mkT)^{3/2}) + (1/2^{3/2})\, (\rho^2 h^6/G^2(2\pi mkT)^3) + \ldots \qquad (14.8.11)$$

Then the velocity distribution f for the Fermi particles is

$$f(v) = G(m/h)^3\, [(1/A)\, e^{-mv^2/2kT} - (1/A^2)\, e^{-2mv^2/2kT} + \ldots]$$

$$= \rho(m/2\pi kT)^{3/2}\, e^{-mv^2/2kT} + (\rho^2 h^3/G(2\pi kT)^3)\, [(1/2^{3/2})\, e^{-mv^2/2kT} - e^{-2mv^2/2kT}] + \ldots \qquad (14.8.12)$$

This equation is valid for a gas, whose degeneracy is small. The condition for this is

$$\rho h^3/G(2\pi mkT)^{3/2} << 1$$

i.e.

$$\rho(m/2\pi kT)^{3/2} << G(m/h)^3$$

(ii) when A is small, (14.8.9) reduces to

$$f(v) = G(m/h)^3$$

Bose particles

In the uniform steady state for Bose particles, we have from (14.8.9)

$$f = G(m/h)^3 / [\, A\, e^{mv^2/2kT} - 1\,] \tag{14.8.13}$$

The constants A in this case is always greater than unity.

14.9. The Law of Corresponding States for Transport Properties

Let us consider a gas of spherical molecules of mass m which are assumed to interact via the intermolecular potential characterised by two parameters σ and ϵ, where σ is the molecular diameter and ϵ the well depth. The transport properties are the functions of the six quantities v, T, m, k, σ and ϵ (v is specific volume, T absolute temperature and k the Boltzmann constant). These quantities can be employed to obtain the laws of the corresponding states for the transport properties such as viscosity, thermal conductivity and diffusion for the classical gases. Thus

$$\eta^* = \eta^* (v^*, T^*) = \eta\, \sigma^2 / (m\epsilon)^{1/2}$$

$$\lambda^* = \lambda^* (v^*, T^*) = \lambda\, \sigma^2\, (m/k)/ (m\epsilon)^{1/2}$$

$$D^* = D^* (v^*, T^*) = D\, \sigma^2\, (m/\sigma^3) / (m\epsilon)^{1/2} \tag{14.9.1}$$

where T^* and v^* are the reduced temperature and reduced specific volume, respectively

$$T^* = kT/\epsilon$$

$$v^* = v/\sigma^3 = V/N\sigma^3 \tag{14.9.2}$$

The functional form of these reduced transport properties depends on the nature of the intermolecular potential energy function.

For the quantum gases, the law of the corresponding states for the transport properties can be written in the form

$$\eta^* = \eta^* (v^*, T^*, \Lambda^*)$$

$$\lambda^* = \lambda^* (v^*, T^*, \Lambda^*)$$

$$D^* = D^* (v^*, T^*, \Lambda^*) \tag{14.9.3}$$

where Λ^* is the quantum mechanical parameter defined by

$$\Lambda^* = h/\sigma\, (m\epsilon)^{1/2} \tag{14.9.4}$$

It is possible to calculate the transport properties of gases from the law of the corresponding states.

Problems

14.1 Derive the Boltzmann transport equation. Discuss its validity.

14.2 Prove that
$(\partial f/\partial t)_{coll} = \int d\Omega \int dv_2 \sigma(\Omega)\, |v_1 - v_2|\, (f_1' f_2' - f_1 f_2)$
where $\sigma(\Omega)$ is the differential scattering cross section.

14.3 State and prove Boltzmann's H theorem.

14.4 Define Boltzmann H function. Explain how the entropy S is related to the H function.

14.5 Show that for an ideal gas in equilibrium, the distribution function is
$f = \rho(m/2\pi kT)^{3/2} \exp[-mv^2/2kT]$
where symbols have their usual meaning.

14.6 An ideal gas is in equilibrium at temperature T. If m be the mass of a molecule and ρ the number density, then show that the H function is
$H = \rho(\ln\rho + (3/2)\,[\ln(m/2kT) - 1])$

14.7 When an ideal gas is in the presence of an external free field **F**, defined by
$F = -\nabla U(r)$
show that the equilibrium distribution function in such a case is
$f = \rho(m/2\pi kT)^{3/2} \exp[\, -((1/2)mv^2 + U)/kT\,]$

14.8 Calculate the mean square fluctuation of velocity $\langle (v - \langle v \rangle)^2 \rangle$ for the Maxwell gas, where
$\langle v^n \rangle = (m/2\pi kT)^{3/2} \int_0^\infty \exp[-(mv^2/2kT)] v^n\, dv$

14.9 Assuming that the molecules of a gas satisfy Maxwell's distribution, calculate the number of molecules crossing a unit area in unit time.

14.10 A gas of relatively low molecular mass interacts with a gas of very heavy molecules. Show that the Boltzmann equation for such a system is
$(\partial f/\partial t)_{coll} = n_H \int (f' - f)\, g_{ij}\, b\, db\, d\phi$
where n_H is the number density of heavy molecules. Calculate the collision rate of a Maxwellian gas molecule.

14.11 What do you understand by the mean free path. Derive an expression for it.

14.12 Derive expressions for η and K. How are they influenced by pressure ? Explain.

14.13 Derive an expression for η for a two-dimensional Maxwellian gas.

CHAPTER 15

DYNAMICAL THEORY OF GASES

In the present chapter we discuss the dynamical properties of fluids and their description in terms of time correlation functions. The thermodynamic quantities of a system have some random fluctuations from their mean values. A study of these fluctuations is of great interest in the nonequilibrium statistical mechanics. It provides a natural framework for understanding some physical phenomena like Brownian motion. The mechanism of the Brownian motion explains how a physical system, which is not in an equilibrium state, finally approaches the equilibrium state. A study of fluctuations also requires the concept of correlation functions. These correlation functions play an important role in providing the dissipative properties of a system.

15.1. Time-Dependent Correlation Functions

The dynamical properties of fluids can be discussed in terms of time dependent correlation functions. The time correlation function of two dynamical variables, $A(t) \equiv A[\mathbf{r}^N(t), \mathbf{P}^N(t)]$ and $B(t) \equiv B[\mathbf{r}^N(t), \mathbf{P}^N(t)]$ may be defined as

$$C_{AB}(\tau) = \langle A(t+\tau)\, B(t) \rangle \tag{15.1.1}$$

where $\langle A(t+\tau)\, B(t) \rangle$ is the ensemble average. We have discussed in chapter 2 that the ensemble average is equal to the time average, so that $\langle A(t+\tau)\, B(t) \rangle$ is expressed as the average over long time, T i.e.

$$\langle A(t+\tau)\, B(t) \rangle = \overline{A(t+\tau)\, B(t)}$$

$$= \lim_{T\to\infty} (1/T) \int_0^T A(t+\tau+t')\, B(t+t')\, dt' \tag{15.1.2}$$

when A = B, the corresponding correlation function is

$$C_A(\tau) = \langle A(t+\tau)\, A(t) \rangle \tag{15.1.3}$$

which is called the time auto-correlation function of quantity A.

When the system is isolated, the correlation function is independent of time origin t and hence stationary with respect to t. Putting t = 0, (15.1.1) can be written as

$$C_{AB}(\tau) = \langle A(\tau)\, B(0) \rangle \equiv \langle A(\tau) B \rangle \tag{15.1.4}$$

For the time correlation function to be stationary,

$$dC_{AB}(\tau)/dt = 0 \tag{15.1.5}$$

which gives

$$(d/dt) \langle A(t+\tau)\, B(t)\rangle = \langle \dot{A}(t+\tau)\, B(t)\rangle + \langle A(t+\tau)\, \dot{B}(t)\rangle = 0 \tag{15.1.6}$$

or

$$\langle \dot{A}(\tau)\, B\rangle = -\langle A(\tau)\dot{B}\rangle \tag{15.1.7}$$

In particular when A = B,

$$\langle \dot{A}A\rangle = 0 \tag{15.1.8}$$

A study of fluctuations is of great physical interest. The time correlation of the fluctuation

$$\delta A(t) = A(t) - \langle A\rangle$$

is defined as

$$C_A(\tau) = \langle \delta A(t+\tau)\, \delta A(t)\rangle \tag{15.1.9}$$

If $\langle A\rangle = 0$, then A (t) denotes the fluctuation of the quantity from its mean value. Thus,

$$C_A(\tau) = \langle A(t+\tau)\, A(t)\rangle \tag{15.1.10}$$

The quantity thus obtained is a function of τ only. In the limiting case $\tau \to \infty$, $C_A(\tau) \to 0$ because there is no correlation between A(t) and A(t+τ). For a slowly varying function, $C_A(\tau)$ tends to zero only for large values of τ, whereas for a rapidly fluctuating function, $C_A(\tau)$ approaches zero at relatively small values of τ. $C_A(\tau)$ is also known as the persistence function of the fluctuation. Correlation functions occur frequently in statistical physics. They have some specific properties of general interest, as mentioned below:

(i) If τ is very large, then A(t) and A(t + τ) become uncorrelated, that is

$$C_A(\tau) \underset{\tau\to\infty}{\to} \langle A(t)\rangle \langle A(t+\tau)\rangle = 0$$

if $\langle A\rangle = 0$.

(ii) For any value of τ, the magnitude of $C_A(\tau)$ cannot exceed the value of $C_A(0)$, i.e.

$$C_A(\tau) \leq C_A(0)$$

In order to prove this relation, we expand the relation

$$\langle |A(t) \pm A(t+\tau)|^2\rangle = \langle A^2(t)\rangle + \langle A^2(t+\tau)\rangle \pm 2\langle A(t)\, A(t+\tau)\rangle = 2[C_A(0) \pm C_A(\tau)] \geq 0$$

consequently, we must have

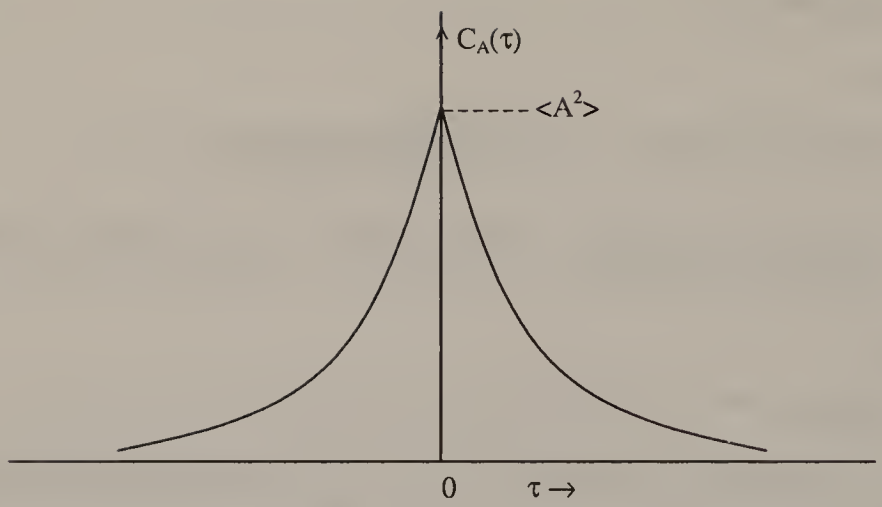


Fig.15.1. The time correlation function $C_A(\tau)$ for the random variable A(t) as a function of the time τ

$$|C_A(\tau)| \leq C_A(0) \qquad \text{for all } \tau$$

(iii) The function $C_A(\tau)$ is symmetric about $\tau = 0$, as shown in Fig. 15.1, i.e.

$$C_A(\tau) = C_A(-\tau)$$

This can be shown by substituting $t \rightarrow t - \tau$. Thus

$$C_A(\tau) = <(A(t)\, A(t+\tau)> = <A(t-\tau)\, A(t)> = <A(t)\, A(t-\tau)> = C_A(-\tau)$$

The Fourier transform of A(t) is defined by

$$A(\omega) = (1/2\pi) \int_{-\infty}^{\infty} A(t) \exp(i\omega t)\, dt \qquad (15.1.11)$$

and the inverse relation by

$$A(t) = \int_{-\infty}^{\infty} A(\omega) \exp(-i\omega t)\, d\omega \qquad (15.1.12)$$

Then, we can write (15.1.10), where $\tau = t_1 - t_2$, as

$$C_A(t_1 - t_2) \equiv <A(t_1)A(t_2)>$$

$$= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \overline{A(\omega)A(\omega')} \exp\,[-i(\omega t_1 + \omega' t_2)] d\omega d\omega' \qquad (15.1.13)$$

We can write

$$A(\omega)A(\omega') = A^2(\omega)\,\delta(\omega+\omega')$$

where $\delta(\omega+\omega')$ is the delta function. Substituting this value and integrating over ω', we get

$$C_A(\tau) \equiv C_A(t_1 - t_2) = \int A^2(\omega)\, e^{-i\omega\tau}\, d\omega \qquad (15.1.14)$$

when $\tau = 0$, we get

$$C_A(0) = \int A^2(\omega)\, d\omega \qquad (15.1.15)$$

which is $\overline{A}^2$, the mean square of the fluctuating quantity, and $A^2(\omega)$ is the spectral density of the mean square fluctuation. From (15.1.14) it is clear that the correlation function $C_A(\tau)$ is the inverse Fourier transform of $A^2(\omega)$. Conversely,

$$A^2(\omega) = (1/2\pi) \int C_A(\tau) \exp(i\omega\tau)\, d\tau \qquad (15.1.16)$$

15.2. Fluctuation and Thermodynamic Properties

It is the mean value of a physical quantity that describes a macroscopic body in equilibrium, and is measured in the equilibrium statistical mechanics. The physical quantity itself deviates from its mean value. The fluctuation of a physical quantity f from its mean value <f> is

$$\Delta f = f - \langle f \rangle \qquad (15.2.1)$$

As we have seen in sec.2.4 the mean fluctuation is

$$\langle \Delta f \rangle = \langle f - \langle f \rangle \rangle = 0$$

and the mean square fluctuation is

$$\langle (\Delta f)^2 \rangle = \langle f^2 \rangle - \langle f \rangle^2 \qquad (15.2.2)$$

The thermodynamic quantities describing a system have small random fluctuation from their mean value.

We shall now calculate the mean square fluctuations of the basic thermodynamic quantities of a system. We begin by deriving a probability distribution law for the fluctuations of these quantities. We consider a physical system A, embedded in a reserviour B (see Fig.4.1), which has the total energy E and the total volume V, where

$$E = E_1 + E_2 = \text{constant}$$

$$V = V_1 + V_2 = \text{constant} \qquad (15.2.3)$$

In equilibrium, the composite system (A + B) has a common temperature T and a common pressure P. Let S(E, V) be the actual value of the entropy of the system. If S_0 is the equilibrium entropy of the system as a function of its mean energy <E> and mean volume, then the fluctuation of entropy from the equilibrium value is

$$\Delta S = S - S_0 = k(\ln \Delta\Gamma - \ln \Delta\Gamma_0) \qquad (15.2.4)$$

where $\Delta\Gamma$ (or $\Delta\Gamma_0$) denotes the statistical weight of the composite system in the presence (or in the absence) of the fluctuation. The probability ρ that the fluctuation may occur in the system, is given by

$$\rho \propto \exp(\Delta S/k) \tag{15.2.5}$$

We can write the fluctuation of entropy ΔS by

$$\Delta S = \Delta S_1 + \Delta S_2 = \Delta S_1 + \int_0^f (dE_2 + P_2 dV_2)/T_2 \tag{15.2.6}$$

where P_2 and T_2 are, respectively, the pressure and temperature of the reservoir, which may, in principle, vary during the fluctuation process. However, the fluctuation will be very small from the point of view of the reservoir, and we can replace P_2 and T_2 by the common values P and T, respectively. Further, from (15.2.3), we have

$$dE_2 = -dE_1$$

$$dV_2 = -dV_1$$

Then (15.2.6) becomes

$$\Delta S = \Delta S_1 - \int_0^f (dE_1 + P dV_1)/T = \Delta S_1 - (\Delta E_1 + P\Delta V_1)/T \tag{15.2.7}$$

and (15.2.5) takes the form

$$\rho \propto \exp[-(\Delta E_1 - T\Delta S_1 + P\Delta V_1)/kT] \tag{15.2.8}$$

Thus the probability distribution law does not depend on the nature of the reservoir in which the system is embedded. In (15.2.8), ΔE_1, ΔS_1 and ΔV_1 are changes in the energy, entropy and volume of the system in fluctuation, and P, T are the pressure and temperature of the medium, i.e. the equilibrium values of the pressure and temperature of the system. Consequently, we may omit the suffix '1' from all quantities and write

$$\rho \propto \exp[-(\Delta E - T\Delta S + P\Delta V)/kT] \tag{15.2.9}$$

Equation (15.2.9) is applicable to any fluctuation. In general, the fluctuation is small, and we can make a Taylor series expansion of ΔE about the equilibrium value $(\Delta E)_0 = 0$. Thus

$$\Delta E = (\partial E/\partial S)_0 \Delta S + (\partial E/\partial V)_0 \Delta V + (1/2)[(\partial^2 E/\partial S^2)_0 (\Delta S)^2 + 2(\partial^2 E/\partial S \partial V)_0 \Delta S \Delta V + (\partial^2 E/\partial V^2)_0 (\Delta V)^2] + \ldots \tag{15.2.10}$$

Using the relations

$$(\partial E/\partial S)_0 = T$$

and

$$(\partial E/\partial V)_0 = -P \tag{15.2.11}$$

Equation (15.2.10) can be written as

$$\Delta E - T\Delta S + P\Delta V = (1/2)\,[(\partial^2 E/\partial S^2)(\Delta S)^2 + 2(\partial^2 E/\partial S\partial V)\,\Delta S\Delta V + (\partial^2 E/\partial V^2)(\Delta V)^2]$$

$$= (1/2)\,[\{((\partial/\partial S)(\partial E/\partial S))_0 \Delta S + ((\partial/\partial V)(\partial E/\partial S))_0 \Delta V\}\Delta S$$

$$+ \{((\partial/\partial S)(\partial E/\partial V))_0 \Delta S + ((\partial/\partial V)(\partial E/\partial V))_0 \Delta V\}\Delta V]$$

$$= (1/2)\,[\Delta T\Delta S - \Delta P\Delta V] \tag{15.2.12}$$

where the following relations have been used

$$\Delta T \equiv \Delta(\partial E/\partial S) = ((\partial/\partial S)(\partial E/\partial S))_0 \Delta S + ((\partial/\partial V)(\partial E/\partial S))_0 \Delta V$$

$$-\Delta P \equiv \Delta(\partial E/\partial V) = ((\partial/\partial S)(\partial E/\partial V))_0 \Delta S + ((\partial/\partial V)(\partial E/\partial S))_0 \Delta V$$

Substituting (15.2.12) in (15.2.9), we obtain the fluctuation probability as

$$\rho \propto \exp[(\Delta P\Delta V - \Delta T\Delta S)/kT\,] \tag{15.2.14}$$

From this we can calculate the fluctuations of various thermodynamic quantities. Let us first choose ΔT and ΔV as the independent variables, then ΔS and ΔP can be written as

$$\Delta S = (\partial S/\partial T)_V \Delta T + (\partial S/\partial V))_T \Delta V = (C_v/T)\,\Delta T + (\partial P/\partial T))_v \Delta V \tag{15.2.15}$$

$$\Delta P = (\partial P/\partial T)_V \Delta T + (\partial P/\partial V))_T \Delta V = (\partial P/\partial T)_V \Delta T - (1/K_T V)\,\Delta V \tag{15.2.16}$$

where

$$(\partial S/\partial V)_T = (\partial P/\partial T)_V$$

and

$$K_T = -(1/V)\,(\partial V/\partial P)_T$$

is the isothermal compressibility. Substituting these values in (15.2.14), we obtain

$$\rho \propto \exp[-(C_v/2kT^2)(\Delta T)^2 - (1/2kTK_T V)\,(\Delta V)^2\,] \tag{15.2.17}$$

This expression shows that the fluctuations of T and V are statistically independent, so that $<\Delta T\Delta V> = 0$. Each term of (15.2.17) represents the Gaussian distribution, thus the mean square fluctuations of T and V are

$$<(\Delta T)^2> = kT^2/C_v$$

$$<(\Delta V)^2> = kTK_T V = -kT(\partial V/\partial P)_T \tag{15.2.18}$$

Similarly, if we choose ΔP and ΔS as the independent variable, then ΔV and ΔT can be expressed as

$$\Delta V = (\partial V/\partial P)_S \Delta P + (\partial V/\partial S)_P \Delta S = K_S V\Delta P + (\partial T/\partial P)_S \Delta S \tag{15.2.19a}$$

$$\Delta T = (\partial T/\partial P)_S \Delta P + (\partial T/\partial S)_P \Delta S = (\partial T/\partial P)_S \Delta P + (T/C_P) \Delta S \quad (15.2.19b)$$

where

$$(\partial V/\partial S)_P = (\partial T/\partial P)_S$$

and

$$K_S = -(1/V)(\partial V/\partial P)_S$$

is the adiabatic compressibility of the system. Substituting these values in (15.2.14), we get

$$\rho \propto \exp[-(K_S V/2kT)(\Delta P)^2 - (1/kC_P)(\Delta S)^2] \quad (15.2.20)$$

In this case, the fluctuation of pressure and entropy are statistically independent, so that

$$<\Delta P \Delta S> = 0$$

and the mean square fluctuation of P and S are

$$<(\Delta P)^2> = kT/K_S V = -kT(\partial P/\partial V)_S$$

$$<(\Delta S)^2> = kC_P \quad (15.2.21)$$

From these formulae we see that the root mean square fluctuations of extensive properties, such as volume and entropy, is proportional to the square root of the size of the system, and the relative fluctuation is inversely proportional to the square root of the size of the system. For intensive properties, such as temperature and pressure, the root mean square fluctuation itself is inversely proportional to the square root of the size of the system. Thus the fluctuations are, in general, thermodynamically small. However, the existence of fluctuations at the microscopic level is of fundamental importance to several macroscopic properties of the system.

Let us now calculate the mean square fluctuation of the energy of the system. If T and V are independent variables, we have,

$$\Delta U = (\partial U/\partial T)_V \Delta T + (\partial U/\partial V)_T \Delta V \quad (15.2.22)$$

Squaring and averaging we obtain

$$<(\Delta U)^2> = [(\partial U/\partial T)_V]^2 <(\Delta T)^2> + [(\partial U/\partial V)_T]^2 <(\Delta V)^2>$$

$$= kT^2 C_v + kTK_T V [(\partial U/\partial V)_T]^2$$

$$= kT^2 C_v + kTK_T (N^2/V) [(\partial U/\partial N)_T]^2 \quad (15.2.23)$$

Equation (15.2.18) give the fluctuation of the volume of the system containing a fixed number N of particles. So the volume fluctuation per particle is obtained by dividing both sides by N^2. Thus,

$$<(\Delta(V/N))^2> = (kT^2 V/N^2) K_T \quad (15.2.24)$$

This fluctuation is true for constant volume, or for constant number of particles. When V is constant,

$$\Delta(V/N) = -(V/N^2)\,\Delta N$$

and (15.2.24) gives

$$<(\Delta N)^2> = (kT^2N^2/V)\,K_T \qquad (15.2.25)$$

Substituting (15.2.25) in (15.2.23), we obtain the result

$$<(\Delta U)^2> = kT^2C_v + <(\Delta N)^2>\,[(\partial U/\partial N)_T^2] \qquad (15.2.26)$$

This formula is applicable to a subsystem with a fixed volume V, and a fluctuating number of particles N.

The results derived above determine the fluctuations of the thermodynamic quantities of a macroscopic subsystem of a given system.

15.3. Brownian Motion

Brownian motion is one of the important subjects of statistical mechanics. In 1827, Robert Brown, a botanist, discovered the incessant motion of tiny pollen immersed in water, when viewed under a high magnifying power microscope. Such a motion of fine particles is demonstrated in Fig.15.2. Particles suspended in a liquid move to and fro, rapidly and continuously, in an entirely haphazard fashion. Such a motion is called Brownian motion, and the particles are referred to as Brownian particles. Brownian motion is a prototype of the random process due to the bombardment of Brownian particles by the molecules of the surrounding fluid.

Fig.15.2. Brownian motion of a fine particle

It was Einstein who first provided a sound theoretical analysis of the Brownian motion on the basis of the random walk problem, and predicted that Brownian motion is due to fluctuations in molecular collisions. Einstein and Smoluchowski worked out the quantitative details of the motion, which were verified experimentally by Perrin.

According to Einstein, the problem of Brownian motion may be looked upon as a problem of diffusion of the Brownian particles through the medium of fluid. If $\rho(\mathbf{r},t)$ be the number density of the Brownian particles in the fluid and $\mathbf{J}(\mathbf{r},t)$ be their current density, then according to Fick's law,

$$\mathbf{J}(\mathbf{r},t) = -D\nabla\rho(\mathbf{r},t) \tag{15.3.1}$$

where D is the diffusion coefficient of the system. The equation of continuity for such a system is

$$(\partial\rho(\mathbf{r},t)/\partial t) + \nabla.\mathbf{J}(\mathbf{r},t) = 0 \tag{15.3.2}$$

Substituting (15.3.1) in (15.3.2), we get the diffusion equation:

$$(\partial\rho(\mathbf{r},t)/\partial t) = D\nabla^2\rho(\mathbf{r},t) \tag{15.3.3}$$

Solution of this equation is

$$\rho(\mathbf{r},t) = (N/(4\pi Dt)^{3/2}) \exp(-r^2/4Dt) \tag{15.3.4}$$

where N is the total number of Brownian particles immersed in the fluid. Equation (15.3.4) is normalised so that

$$\int_0^\infty \rho(\mathbf{r},t)\, 4\pi r^2\, dr = N \tag{15.3.5}$$

Equation (15.3.4) can be used to calculate the ensemble averages of physical quantities. Thus, we have

$$\langle r^2(t)\rangle = (4\pi/N) \int_0^\infty \rho(\mathbf{r},t)\, r^4\, dr = (4\pi/(4\pi Dt)^{3/2}) \int_0^\infty \exp(-r^2/4Dt)\, r^4\, dr = 6Dt \tag{15.3.6}$$

In one-dimensional problems, where

$$\rho(x,t) = (N/(4\pi Dt)^{1/2}) \exp(-x^2/4Dt) \tag{15.3.7}$$

the mean square value $\langle x^2\rangle$ is

$$\langle x^2\rangle = 2\,Dt \tag{15.3.8}$$

Thus the ensemble of Brownian particles is initially concentrated at the origin, and diffuses out as time increases. The diffusion process is irreversible. In this case the irreversible character of the phenomenon arises from the random fluctuating forces exerted by the fluid molecules on the Brownian particles. This lead Langevin (1908) to develop a promising theory of the Brownian motion.

15.4. Langevin Theory

Langevin developed a simple theory for the Brownian motion of particles, which arises from molecular collisions. The collisions exert random, unbalanced force on the particle. Let $\mathbf{X}(t)$ be the force acting on the particle, then the equation of motion of a particle of mass m, suspended in a liquid, is

$$m\,(dv/dt) = \mathbf{X}(t) \tag{15.4.1}$$

where v(t) is the particle velocity. In the present case the mean value of the fluctuating force $\mathbf{X}(t)$ may or may not be zero. Langevin made the important assumption that the force $\mathbf{X}(t)$ may be written as a sum of two parts

$$\mathbf{X}(t) = -\beta m v + \mathbf{F}(t) \tag{15.4.2}$$

where $-\beta mv$ represents the viscous drag on the particle moving with velocity v, and $\mathbf{F}(t)$ represents the rapidly fluctuating force due to molecular collisions, which, over long interval of time, averages out to zero. Thus

$$m\,(dv/dt) = -\beta m v + \mathbf{F}(t)$$

$$\overline{\mathbf{F}(t)} = 0 \tag{15.4.3}$$

The viscous force is assumed to be given by Stokes' law. For a spherical particle of radius a moving in a medium of viscosity η, Stoke's law gives

$$\beta m = 6\pi a\eta \tag{15.4.4}$$

Taking the ensemble average of (15.4.2), we get

$$m\,(d/dt)\langle v\rangle = -\beta m\langle v\rangle \tag{15.4.5}$$

which gives

$$\langle v(t)\rangle = v(0)\exp(-t/\tau_c) \tag{15.4.6}$$

where $\tau_c = \beta^{-1}$ is the relaxation time. Thus the drift velocity of the particle decays to the zero value.

Dividing throughout by m, (15.4.3) can be written as

$$dv/dt = -\beta v + A(t) \tag{15.4.7}$$

We multiply (15.4.7) by x, so that

$$\ddot{x}x = -\beta\dot{x}x + xA(t) \tag{15.4.8}$$

Now,

$$(d/dt)(x^2) = 2\dot{x}x$$

$$(d^2/dt^2)(x^2) = 2\ddot{x}x + 2(\dot{x})^2$$

thus,

$$\ddot{x}x = (1/2)(d^2/dt^2)(x^2) - (\dot{x})^2$$

Using these relations, we have from (15.4.8)

$$(1/2)(d^2/dt^2)(x^2) - (\dot{x})^2 = -(1/2)\,\beta\,(d/dt)\,(x^2) + xA(t) \tag{15.4.9}$$

We now take the time average of this equation. We assume

$$\overline{xA(t)} = 0$$

because A(t) is a random force of average zero, and it is uncorrelated to x. Thus we get

$$(1/2)(d^2/dt^2)\langle x^2\rangle + (1/2)\,\beta\,(d/dt)\,\langle x^2\rangle = \langle \dot{x}^2 \rangle \tag{15.4.10}$$

The Brownian particles are assumed to attain thermal equilibrium with the molecules of the fluid, so their mean kinetic energy can be given by the equilibrium theorem

$$(1/2)\,m\,(\dot{x}^2) = (1/2)\,kT$$

where T is the absolute temperature. Thus

$$(d^2/dt^2)\langle x^2\rangle + \beta(d/dt)\,\langle x^2\rangle = 2kT/m \tag{15.4.11}$$

Let

$$(d/dt)\langle x^2\rangle = y$$

then (15.4.11) takes the form

$$(dy/dt) + \beta y = 2kT/m$$

or

$$dy/dt = -\beta(y - 2kT/m\beta)$$

On integration, we get

$$y \equiv (d/dt)\,\langle x^2\rangle = (2kT/m\beta) + C\,e^{-\beta t} \tag{15.4.12}$$

where C is a constant, which can be evaluated with the conditions that at $t = 0$ both $\langle x^2\rangle$ and $(d/dt)\langle x^2\rangle$ vanish. Thus we obtain the results

$$(d/dt)\,\langle x^2\rangle = (2kT\tau_c/m)\,[1 - e^{-t/\tau_c}] \tag{15.4.13}$$

and

$$\langle x^2\rangle = (2kT\tau_c^2/m)\,[(t/\tau_c) - (1 - e^{-t/\tau_c})] \tag{15.4.14}$$

The transient state is given by the exponential term.

When $t \ll \tau_c$, we obtain the steady state situation

$$\langle x^2\rangle \quad (kT/m)\,t^2 = \langle v^2\rangle\,t^2 \tag{15.4.15}$$

which is consistent with the reversible equation of motion. This shows that the particle begins to move with thermal velocity $(kT/m)^{1/2}$.

On the other hand, when $t \gg \tau_c$ the Brownian motion sets in as a result of random collisions, and we obtain

$$\langle x^2 \rangle = (2kT\tau_c/m)\, t = (2kT/m\beta)\, t \qquad (15.4.16)$$

For the special case of spherical particles, where the Stokes law gives the value of β, this gives

$$\langle x^2 \rangle = (kT/3\pi a\eta)\, t \qquad (15.4.17)$$

i.e.

$$\langle x^2 \rangle \propto t$$

as expected for a random walk. This equation was originally derived by Einstein.

Comparing (15.3.7) and (15.4.16) we obtain a relation

$$D = (kT/m\beta) = BkT \qquad (15.4.18)$$

where B is the mobility of the system. Equation (15.4.18) is generally referred to as the Einstein relation.

15.5. Power Spectrum of Fluctuations : The Wiener-Khintchine Theorem

We have already seen that the physical quantity A(t) varies with time t, fluctuating about its mean value $\langle A \rangle \equiv A_0$ as shown in Fig.2.2, and predicting the spectral characteristic of a fluctuation pattern. We shall discuss a technique of analysis the time scale of the fluctuation. Suppose we consider the fluctuating quantity A(t) for a long interval $0 < t < T$. Such a fluctuation can be expressed in a Fourier series as

$$A(t) = \sum_{n=0}^{\infty} [a_n \cos \omega_n t + b_n \sin \omega_n t] \qquad (15.5.1)$$

where

$$a_n = (2/T) \int_0^T A(t) \cos(\omega_n t)\, dt \qquad (15.5.2a)$$

$$b_n = (2/T) \int_0^T A(t) \sin(\omega_n t)\, dt \qquad (15.5.2b)$$

and

$$\omega_n = 2\pi n/T$$

We assume that the mean square value $\langle (A(t))^2 \rangle$ has attained an equilibrium, or stationary value i.e.

$$\langle (A(t))^2 \rangle = \text{constant}$$

Such a quantity is said to be statistically stationary. When the physical quantity is more or less a random function of time, then the Fourier coefficients are statistical in nature.

The time average of $[A(t)]^2$, denoted by $\overline{[A(t)]^2}$, is

$$\overline{[A(t)]^2} = (1/T) \int_0^T (\Sigma_n [a_n \cos \omega_n t + b_n \sin \omega_n t])^2\, dt = (1/2) \Sigma_n [a_n^2 + b_n^2] \qquad (15.5.3)$$

because

$$\overline{\cos \omega_n t \cos \omega_m t} = 1/2 \quad \text{if } n = m$$

$$= 0 \quad \text{if } n \neq m$$

$$\overline{\sin \omega_n t \sin \omega_m t} = 1/2 \quad \text{if } n = m$$

$$= 0 \quad \text{if } n \neq m$$

$$\overline{\cos \omega_n t \sin \omega_m t} = 0 \quad \text{for all n and m} \qquad (15.5.4)$$

Next, the measurement are made on a large number of systems in the ensemble. Taking the ensemble average of (15.5.3), we get

$$\langle \overline{[A(t)]^2} \rangle = (1/T) \sum_n [\langle a_n^2 \rangle + \langle b_n^2 \rangle] \qquad (15.5.5)$$

The amount of power contained in a frequency $\nu_n = n/T$ is

$$(1/2) [\langle a_n^2 \rangle + \langle b_n^2 \rangle]$$

Due to randomness of the phases of various components, we have for all n,

$$\langle a_n^2 \rangle = \langle b_n^2 \rangle$$

and (15.5.5) can be written as

$$\langle \overline{[A(t)]^2} \rangle = \sum_n \langle a_n^2 \rangle \qquad (15.5.6)$$

When T is large, the separation between two frequencies may be taken as very small.

If $\Delta\nu_n$ be a frequency bandwidth, which is equal to the separation between two adjacent frequencies, i.e

$$\Delta\nu_n = \nu_{n+1} - \nu_n = 1/T$$

then we have

$$\langle A^2 \rangle = \sum_n G(\nu_n) \Delta\nu_n \quad \int_0^\infty G(\nu)\, d\nu \qquad (15.5.7)$$

where

$$\langle a_n^2 \rangle = G(\nu_n) \Delta\nu_n \qquad (15.5.8)$$

$G(\nu)$ is called the special density of the randomly fluctuating quantity A(t), (15.5.7) represents the power spectrum of A(t)

Now it is easy to calculate the auto-correlation function $C_A(\tau)$ in terms of $G(\nu)$. For this we consider the correlation function

$$C_A(\tau) = \overline{A(t)\, A(t+\tau)} \qquad (15.5.9)$$

where the average is over time t. We may take an ensemble average of the time average, so that

$$C_A(\tau) = \overline{\langle A(t)\, A(t+\tau)\rangle}$$

$$= \left\langle (1/T) \int_0^T (\Sigma_n [a_n \cos \omega_n t + b_n \sin \omega_n t])\, (\Sigma_m [a_m \cos \omega_m (t+\tau) + b_m \sin \omega_m (t+\tau)])\, dt \right\rangle \tag{15.5.10}$$

Using the expansions

$$\sin\omega_m(t+\tau) = \sin\omega_m t \cos\omega_m \tau + \cos\omega_m t \sin\omega_m \tau$$

$$\cos\omega_m(t+\tau) = \cos\omega_m t \cos\omega_m \tau - \sin\omega_m t \sin\omega_m \tau$$

and with the help of (15.5.3), (15.5.9) can be evaluated to give

$$C_A(\tau) = (1/2) \sum_n [\langle a_n^2 \rangle + \langle b_n^2 \rangle] \cos\omega_m \tau = \sum_n \langle a_n^2 \rangle \cos\omega_n \tau \tag{15.5.11}$$

Using (15.5.8), we obtain

$$C_A(\tau) = \sum_n G(\nu_n)\, \Delta\nu_n \cos 2\pi\nu_n \tau \int_0^\infty G(\nu) \cos 2\pi\nu\tau\, d\nu \tag{15.5.12}$$

This equation establishes a relation between the correlation function and the power spectrum of the fluctuations.

When $\tau = 0$, (15.5.12) yields the important result

$$C_A(0) = \int_0^\infty G(\nu)\, d\nu = \langle A^2 \rangle \tag{15.5.13}$$

Equation (15.2.12) gives the correlation function in the Fourier cosine transform of the power spectrum. The inverse relation is

$$G(\nu) = 4 \int_0^\infty C_A(\tau) \cos 2\pi\nu\tau\, d\tau \tag{15.5.14}$$

Equation (15.5.14) together with (15.5.12) is called the Wiener-Khintchine theorem.

The Wiener-Khintchine theorem has an obvious physical content. It tells us how rapidly the random process is changing. For example, let the fluctuations decay exponentially with time, so that

$$C_A(\tau) = C_A(0) \exp(-\tau/\tau_c) \tag{15.5.15}$$

where τ_c is a relaxation time, which is a measure of the time average, the system exists without changing its state. Variation of $C_A(\tau)$ with τ is shown in Fig.15.3.

Substituting this value of $C_A(\tau)$ in (15.5.14), we get

$$G(\nu) = 4\, C_A(0) \int_0^\infty \cos(2\pi\nu\tau) \exp(-\tau/\tau_c)\, d\tau \qquad (15.5.16)$$

Making use of the integral

$$\int_0^\infty e^{-\alpha x} \cos\beta x\, dx = \mathrm{Re} \int_0^\infty e^{-(\alpha - i\beta)x}\, dx = \mathrm{Re}\, [e^{-(\alpha - i\beta)x} / -(\alpha - i\beta)]_0^\infty = \mathrm{Re}\, [1/(\alpha - i\beta)]$$

$$= \mathrm{Re}\, [(\alpha + i\beta)/(\alpha^2 + \beta^2)] = \alpha / (\alpha^2 + \beta^2)$$

where 'Re' denotes the real part of the integral. (15.5.6) can be evaluated as

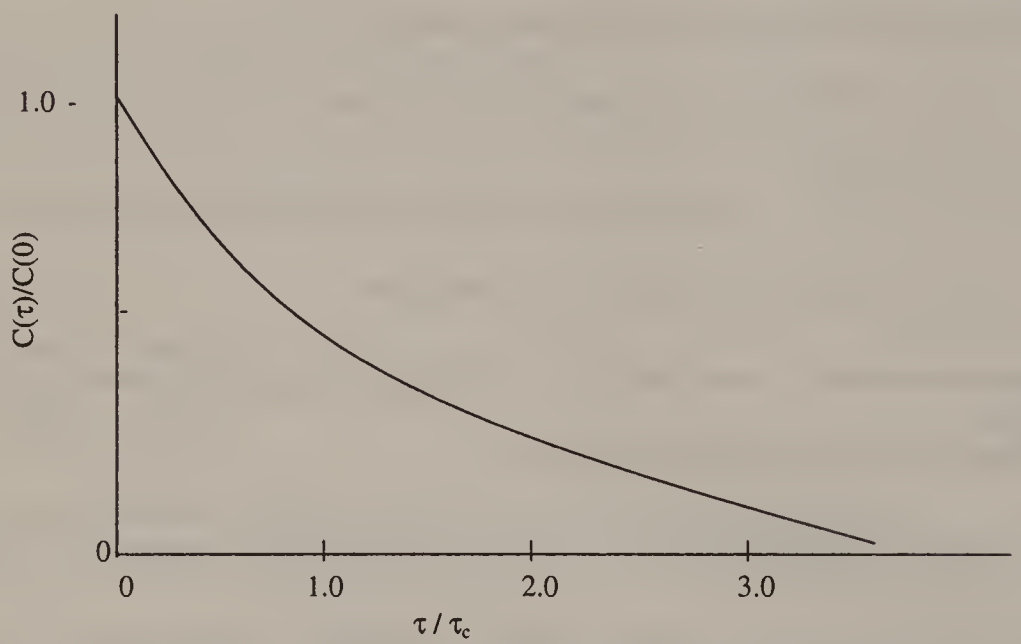


Fig.15.3. The correlation function $C_A(\tau)$ decays exponentially with time τ

$$G(\nu) = 4\, C(0)\, \tau_c / (1 + 4\pi^2\nu^2\tau^2) = G(0) / (1 + 4\pi\nu^2\tau_c^2) \qquad (15.5.17)$$

which is shown in Fig.15.4. The power spectrum is flat for frequencies much less than $(1/2\pi\tau_c)$, but rapidly decreases to zero at high frequencies.

The Wiener-Khintchine theorem has wide applications. For example, it can be used to study the fluctuation in electrical and electronic systems.

15.6 Nyquist Theorem

The Nyquest theorem is of great importance in electronic physics. The Brownian motion of electrons in matter generates a fluctuating voltage across a sample of matter. This effect is commonly known as Johnson or thermal noise. The Nyquist theorem gives a quantitative expression for the thermal noise. According to this theorem, the mean square voltage across a resistance R in thermal equilibrium at temperature T, and for a frequency range dv, is given by

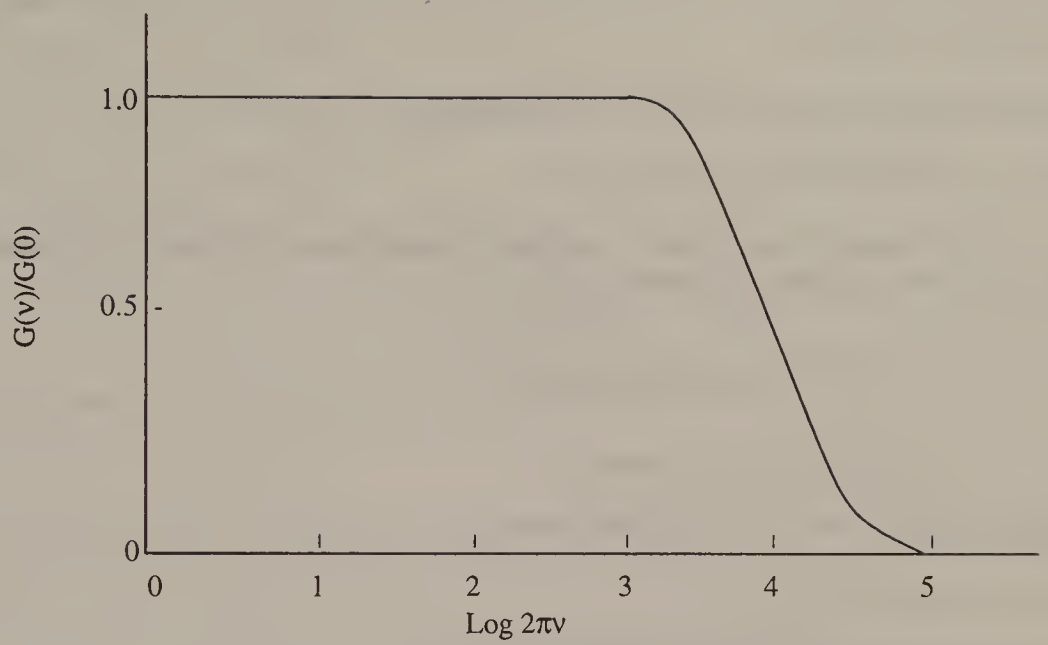


Fig.15.4. The spectral density G(ν) for an exponential correlation function $C_A(\tau)$

$$\langle V^2 \rangle \Delta\nu = 4RkT\Delta\nu \tag{15.6.1}$$

where $\Delta\nu$ is the frequency bandwidth within which the voltage fluctuation are measured.

We can derive the Nyquist theorem on a microscopic basis, using the Wiener-Khintchine theorem. Let us consider a resistor of resistance R, with area a and length l. Let n be the electrons per unit volume of the resistor. We assume that the electrons obey Maxwell-Boltzmann statistics. If $\langle v \rangle$ be the mean drift velocity of the electrons under an applied field E, then the current density $j = ne\langle v \rangle$, and the current $I = aj = ane\langle v \rangle$, where e is the charge of an electron.

The voltage across the resistor is

$$V = RI = R\, ane \langle v \rangle \tag{15.6.2}$$

The total number of electrons in the specimen is nal, so that

$$nal \langle v \rangle = \sum_i v_i \tag{15.6.3}$$

where summation is over all electrons. Thus, we get

$$V = (Re/l) \sum_i v_i = \sum_i V_i \tag{15.6.4}$$

where

$$V_i = Rev_i/l \tag{15.6.5}$$

Now v_i is a random variable, and so is V_i

Let G(ν) be the spectral density of the voltage fluctuation across the specimen, then in the frequency range $\Delta\nu$,

$$\langle V^2 \rangle \Delta\nu = G(\nu)\Delta\nu \tag{15.6.6}$$

The velocity correlation function in this case can be written as

$$C(\tau) = \overline{\langle v_i(t+\tau)\, v_i(t) \rangle} = \langle v_i^2 \rangle \exp(-\tau/\tau_c) \tag{15.6.7}$$

where τ_c is the relaxation time, which is the mean interval between successive collisions. Then according to the Wiener-Khintchine theorem, we have

$$G_i(\nu) = 4(Re/l)^2 \langle v_i^2 \rangle \int_0^\infty \exp(-\tau/\tau_c) \cos 2\pi\nu\tau \, d\tau$$

$$= 4(Re/l)^2 \langle v_i^2 \rangle (\tau_c/(1 + (2\pi\nu\tau_c)^2)) \tag{15.6.8}$$

Under normal condition, $\nu\tau_c \ll 1$, and (15.6.8) reduces to

$$G_i(\nu) = 4(Re/l)^2 \langle v_i^2 \rangle \tau_c \tag{15.6.9}$$

At equilibrium, in accordance with the equipartition theorem,

$$\langle v_i^2 \rangle = kT/m$$

Then the power spectrum of the voltage across the resistor is

$$G(\nu) = nal\, G_i = 4\, na\, R^2 e^2\, \tau_c\, kT / lm \tag{15.6.10}$$

The resistance of the resistor is

$$R = l/\sigma a = lm/ne^2\, a\, \tau_c \tag{15.6.11}$$

where

$$\sigma = ne^2\tau_c/m$$

is the conductivity. Using the value of R, we get

$$G(\nu) = 4\, RkT \tag{15.6.12}$$

and hence in the frequency range $\Delta\nu$

$$\langle V^2 \rangle \Delta\nu = 4\, RkT\Delta\nu \tag{15.6.13}$$

which is the desired result, i.e. the Nyquist theorem. This was first discovered empirically by Johnson in 1927, and later derived by Nyquist on the basis of thermodynamic considerations.

15.7. Fluctuation-Dissipation Theorem

When tiny macroscopic bodies are immersed in a fluid, they are continuously bombarded by the fluid particles, which ultimately bring the motion to a stop. The kinetic energy of the bodies is thereby converted into heat, and is said to be dissipated. The microscopic interactions are associated with the fluctuations in the motion of the bodies. Naturally, the fluctuations affect the motion of the bodies through the mechanism of energy dissipation. We consider the relationship between the fluctuation and the energy dissipation, known as the fluctuation-dissipation theorem.

We start with the Langevin equation for one-dimensional Brownian motion [see Eq.(15.4.7)],

$$dv(t')/dt' = -\beta v(t') + A(t') \tag{15.7.1}$$

Multiplying both sides by $e^{(\beta t')}$ and rearranging, we get

$$d/dt' \, (e^{\beta t'} v(t')) = e^{\beta t'} A(t)$$

On integration between limits, t' = 0 and t' = t, we obtain

$$v(t) = v(0) \exp(-\beta t) + \exp(-\beta t) \int_0^t \exp(\beta t') A(t') \, dt' \tag{15.7.2}$$

From this equation, the average drift velocity is given by

$$\langle v(t) \rangle = v(o) \exp(-\beta t) \tag{15.7.3}$$

since $\langle A(t') \rangle = 0$ for all t'. This is same as the earlier result (15.4.6). We use (15.7.2) to calculate the mean square velocity $\langle v^2(t) \rangle$. Thus

$$\begin{aligned} \langle v^2(t) \rangle &= v^2(0) \exp(-2\beta t) + 2\exp(-2\beta t) \, v(0) \int_0^t \exp(\beta t') \langle A(t') \rangle \, dt' \\ &\quad + \exp(-2\beta t) \int_0^t \int_0^t \exp[\beta(t'+t'')] \langle A(t') \, A(t'') \rangle \, dt'dt'' \\ &= v^2(0) \exp(-2\beta t) + \exp(-2\beta t) \int_0^t \int_0^t \exp[\beta(t'+t'')] \, C_A(t',t'') \, dt'dt'' \end{aligned} \tag{15.7.4}$$

where

$$C_A(t',t'') = \langle A(t') \, A(t'') \rangle = \langle A(t') \, A(t' + s) \rangle = C_A(s) \tag{15.7.5}$$

is the time auto-correlation function of the variable A. It is measure of the statistical correlation between the values of the fluctuating quantity A at times t' and t''. The fluctuation-dissipation theorem, which we derive below, is a statement about the double time integral of $C_A(s)$.

We now evaluate the double integral over $C_A(s)$ in (15.7.4). Changing over to the variables

$$\begin{aligned} u &= (1/2) \, (t' + t'') \\ s &= t'' - t' \end{aligned} \tag{15.7.6}$$

we obtain the result

$$I = \int_0^t \int_0^t \exp[\beta(t'+t'')] \, C_A(s) \, dt'dt'' = \int_{-\infty}^{\infty} ds \, C_A(s) \int_0^t \exp(2\beta u) \, du = (2\beta)^{-1} \, [\exp(2\beta t) - 1] \, K \tag{15.7.7}$$

where

$$K = \int_{-\infty}^{\infty} ds \, C_A(s) = \int_{-\infty}^{\infty} ds \, \langle A(0) \, A(s) \rangle = (1/m^2) \int_{-\infty}^{\infty} ds \, \langle F(0) \, F(s) \rangle \tag{15.7.8}$$

Substituting (15.7.7) in (15.7.4), we obtain

$$\langle v^2(t) \rangle = v^2(0) \exp(-2\beta t) + (K/2\beta) \, [1 - \exp(-2\beta t)] \tag{15.7.9}$$

In the limit $t \to \infty$, the system attains the equilibrium state, where

$$\langle v^2(t) \rangle = kT/m$$

Thus, we have from (15.7.9)

$$K = (2kT\beta/m) \tag{15.7.10}$$

Comparing (15.7.8) and (15.7.10), we have

$$\alpha = \beta m = (1/2kT) \int_{-\infty}^{\infty} ds \langle F(0)\, F(s) \rangle = (m^2/2kT) \int_{-\infty}^{\infty} ds \langle v(0)\, v(s) \rangle \tag{15.7.11}$$

This equation for the damping constant α is the fluctuation-dissipation theorem for Brownian motion. Then (15.7.9) takes the form

$$\langle v^2(t) \rangle = v^2(0) + [(kT/m) - v^2(0)][1 - \exp(-2\beta t)] \tag{15.7.12}$$

If $v^2(0) = kT/m$, then $\langle v^2(t) \rangle = kT/m$. This shows that statistical equilibrium, once attained, has a natural tendency to persist. We note that if the random force F(t) which produces fluctuations is large, the interaction between the macroscopic body and its medium is strong. In this case it is plausible that there exists a relation between fluctuation and dissipation. But in the presence of strong interaction, the system will rapidly come to equilibrium if it is not in equilibrium initially. This situation is governed by the dissipation constant α. Thus the fluctuation-dissipation theorem establishes a relation between two opposing tendencies of common origin, and characterised by $C_A(s)$ and α.

15.8. Fokker-Planck Equation

In this section the problem of time dependence of the fluctuating quantity is considered in a more general way. We derive a differential equation, known as the Fokker-Planck equation for the probability f(v,t) that a particle has a velocity v at a time t. For the sake of simplicity, we consider here a one-dimensional velocity distribution. However, the technique is applicable to any fluctuating quantity.

At any time t, let f(v,t)dv be the probability that a particle in the ensemble has a velocity between v and v + dv. The function f(v,t) must satisfy the normalisation condition

$$\int_{-\infty}^{\infty} f(v,t)\, dv = 1 \tag{15.8.1}$$

If P(v,v') dv' be the probability that a particle having a velocity v at time t makes a transition to be a particle having velocity between v' and v'+dv' after a time interval τ, then the velocity distribution at time $t + \tau$ will be

$$f(v, t+\tau) = \int_{-\infty}^{\infty} f(v - \xi, t)\, P(v-\xi, \xi)\, d\xi \tag{15.8.2}$$

where

$$\xi = v' - v \equiv v(t+\tau) - v(t)$$

We assume that in the small interval τ, the velocities change only by a small amount so that transition probability function P(v,v') is sharply peaked around $v' \ll v$, and falls rapidly to zero elsewhere. Therefore, we can expand $f(v - \xi, t)$ and $P(v - \xi, \xi)$ in powers of ξ. Retaining terms up to the second order, we obtain

$$f(v-\xi, t) = f(v,t) - \xi\,(\partial f(v,t)/\partial v) + (1/2)\,\xi^2\,(\partial^2 f(v,t)/\partial v^2)$$

$$P(v-\xi, \xi) = P(v, \xi) - \xi\,(\partial P(v, \xi)/\partial v) + (1/2)\xi^2\,(\partial^2 P(v,\xi)/\partial v^2) \qquad (15.8.3)$$

Expanding $f(v, t+\tau)$ in powers of τ, we also obtain

$$f(v, t+\tau) = f(v,t) + \tau(\partial f(v,t)/\partial t) \qquad (15.8.4)$$

Substituting these values in (15.8.2), we obtain

$$\partial f/\partial t = -[f(\partial\gamma/\partial v) + (\partial f/\partial v)\gamma] + (1/2)\,[f(\partial^2\delta/\partial v^2) + 2(\partial f/\partial v)(\partial\delta/\partial v) + (\partial^2 f/\partial v^2)\delta]$$

$$= -(\partial/\partial v)(\gamma f) + (1/2)\,(\partial^2/\partial v^2)\,(\delta f) \qquad (15.8.5)$$

where, due to normalisation condition for $P(v, \xi)$

$$\int_{-\infty}^{\infty} P(v, \xi)\, d\xi = 1 \qquad (15.8.6)$$

and

$$A_1(v) \equiv \tau\gamma \equiv \int_{-\infty}^{\infty} \xi P(v, \xi)\, d\xi = \langle\xi\rangle \qquad (15.8.7)$$

$$A_2(v) \equiv \tau\delta \equiv \int_{-\infty}^{\infty} \xi^2 P(v, \xi)\, d\xi = \langle\xi^2\rangle \qquad (15.8.8)$$

Here $A_1(v)$ and $A_2(v)$ are, respectively, the first and second moments of the velocity increments. Equation (15.8.5) is a partial differential equation for the velocity distribution function, known as the Fokker-Planck equation. It plays an important role in the theory of fluctuations, and Brownian motion. The equation is applicable to a great variety of random processes for calculation of the probability density of a transition. If the probability function is a symmetric function of ξ, the first moment is zero, i.e.

$$A_1(v) = 0$$

Further, if we assume that $A_2(v)$ is independent of velocity, the Fokker-Planck equation reduces to

$$\partial f/\partial t = (\delta/2)\,(\partial^2 f/\partial v^2) \qquad (15.8.9)$$

This is identical to the usual diffusion equation with diffusion coefficient $D = \delta/2$. Let us apply this equation to an ensemble of particles with initial velocity v_0. In view of the solution (15.8.7), the function $f(x,t)$ will be

$$f(v,t) = (1/(4\pi Dt)^{1/2})\,\exp\,[-(v - v_0)^2/4Dt] \qquad (15.8.10)$$

The mean square deviation of velocity of a particle from the initial velocity v_0 during the time interval τ is of particular interest in this case.

$$\langle(v - v_0)^2\rangle = \int_{-\infty}^{\infty} (v-v_0)^2\, f(v, \tau)\, dv = (4\pi D\tau)^{1/2} \int_{-\infty}^{\infty} (v-v_0)^2\, \exp[-(v-v_0)^2/4D\tau]\, dv$$

$$= 2D\tau = 2kT/m\beta \qquad (15.8.11)$$

We now consider the Fokker-Planck equation for Brownian particles. The Langevin equation for such

a particle is

$$dv/dt = -\beta v + A(t) \tag{15.8.12}$$

Integrating over a small interval τ, we get

$$\xi = v(t+\tau) - v(t) = -\beta v\tau + K(\tau) \tag{15.8.13}$$

where

$$K(\tau) = \int_t^{t+\tau} A(t')\, dt' \tag{15.8.14}$$

Since A(t') is a random variable of average zero

$$\langle K \rangle = 0$$

and hence,

$$\langle \xi \rangle = -\beta v\tau \tag{15.8.15}$$

Following the method discussed in Sec.15.7, it can be shown that

$$\langle [v(t+\tau) - v(t) \exp(-\beta\tau)]^2 \rangle = (K/2\beta)\,[1 - \exp(-2\beta\tau)] = (KT/m)\,[1 - \exp(-2\beta\tau)]$$

which can be expanded as

$$\langle \xi^2 \rangle + 2\langle \xi \rangle \langle v(t) \rangle\,[1 - \exp(-\beta\tau)] + \langle v^2(t) \rangle\,[1 - \exp(-\beta\tau)]^2 = (KT/m)\,[1 - \exp(-2\beta\tau)]$$

In the limit $\tau \ll \beta^{-1}$, it can be reduced to

$$\langle \xi^2 \rangle = (2kT\beta/m)\tau + 0(\tau^2) \tag{15.8.16}$$

Thus for a Brownian particle

$$\gamma = -\beta v$$

$$\delta = 2kT\beta/m = 2D_0 \tag{15.8.17}$$

and the Fokkèr-Planck equation becomes

$$\partial f/\partial t = \beta f + Bv(\partial f/\partial v) + D_0(\partial^2 f/\partial v^2) \tag{15.8.18}$$

Let us apply this equation to an ensemble of Brownian particles with initial velocity v_o at t = 0. In order to solve this equation, we introduce a new variable

$$s = v \exp(\beta t)$$

then,

$$f(v,t) = f[s \exp(-\beta t), t] = R(s,t) \exp(\beta t) \tag{15.8.19}$$

On differentiation we get,

$$\partial f/\partial v = (\partial f/\partial s)\,(\partial s/\partial v) = e^{2\beta t}\,(\partial R/\partial s)$$

$$\partial^2 f/\partial v^2 = (\partial s/\partial v)\,(\partial/\partial s)(e^{2\beta t}(\partial R/\partial s)) = e^{3\beta t}\,(\partial^2 R/\partial s^2)$$

$$\partial f/\partial v = (\partial f/\partial t) + (\partial f/\partial s)(\partial s/\partial t) = \beta e^{\beta t} R + e^{\beta t}(\partial R/\partial t) + \beta v e^{2\beta t}(\partial R/\partial s)$$

Substituting these values in (15.8.18), we get

$$\partial R/\partial t = D_0 e^{\beta t}(\partial^2 R/\partial s^2) \tag{15.8.20}$$

which can be further simplified by introducing a variable

$$\theta = (2\beta)^{-1}[\exp(2\beta t) - 1]$$

Then,

$$\partial R/\partial t = (\partial\theta/\partial t)(\partial R/\partial\theta) = e^{2\beta t}(\partial R/\partial\theta)$$

and (15.8.20) becomes

$$\partial R/\partial\theta = D_0(\partial^2 R/\partial s^2) \tag{15.8.21}$$

which is the one-dimensional diffusion equation. The solution of this equation is

$$R(s, \theta) = (4\pi D_0\theta)^{-1/2} \exp[-(s - v_0)^2/4D_0\theta] \tag{15.8.22}$$

Hence the general solution of (15.8.18) is given by

$$f(v,t) = [m/2\pi kT(1 - e^{-2\beta t})]^{1/2} \exp[m(v - v_0 e^{-\beta t})^2/2kT(1 - e^{-\beta t})] \tag{15.8.23}$$

In the limit $\beta \to 0$, (15.8.23) reduces to (15.8.10) which is a purely diffusive situation. On the other hand, when $t \gg \beta^{-1}$, it tends to a Maxwellian distribution of speeds, i.e

$$f(v,t) = (m/2\pi kT)^{1/2} \exp(-mv^2/2kT) \tag{15.8.24}$$

Thus, as time progress, an ensemble of Brownian particles approaches a state of equilibrium under the influence of the restoring force and the molecular collisions.

15.9. Spatial Correlations of Fluctuations for an Ideal Gas

Lastly we discuss some specific properties of the spatial correlation functions for an ideal gas. We have discussed the spatial correlation function for a classical system in the previous chapters. In this section we are interested only in the ideal gas.

We consider a homogeneous, isotropic system, such as gas or liquid in which all positions of the particles in space are equally probable for any given particle. A given particle may be at any point $\mathbf{r}$ in the space with the condition that all other particles can occupy arbitrary positions. For example, if we consider two particles simultaneously, then for a given position of one particle, the second particle may occupy different positions. These positions of the second particle will not be equally probable, and the relative position $(\mathbf{r}_2\text{-}\mathbf{r}_1)$ of the two particles will have different values. There is no correlation between the particles when they are far apart. Thus for a system of noninteracting particles, the distribution function is

$$n_N(\mathbf{r}_1, \mathbf{r}_2) = n_N(\mathbf{r}_1)\, n_N(\mathbf{r}_2) = \rho^2$$

where $n_N(\mathbf{r}_1) = n_N(\mathbf{r}_2) = \rho$ for a homogeneous fluid. Due to the interaction potential, there exists in general a correlation between the simultaneous positions $\mathbf{r}_1$ and $\mathbf{r}_2$ of the two particles. Thus one can write (see Eq.(9.7.4))

$$n_N(\mathbf{r}_1, \mathbf{r}_2) = n_N(\mathbf{r}_1)\, n_N(\mathbf{r}_2)\, g(\mathbf{r}_1, \mathbf{r}_2) = \rho^2 g(r) \tag{15.9.1}$$

where $r = |r_2 - r_1|$, and g(r) is the pair distribution function. This function has been discussed in detailed in Sec.9.7. In case of a noninteracting classical gas, there is no spatial correlation, and we have

$$g(r) = 1$$

For real systems g(r) is generally different from unity. In order to measure the deviation of the pair distribution function from unity, we introduce the pair correlation function h(r) defined by the relation (see Eq.(9.7.9))

$$h(r) = g(r) - 1 \tag{15.9.2}$$

The mean squa. fluctuation of the density of the system can be expressed as the space integral of the correlation functi.on h(r), as discussed in Sec.11.2. For a noninteracting classical gas, the correlation function is

$$h(r) = 0$$

Thus in case of an ideal classical gas, there is no correlation between the positions of various particles. However, in an ideal quantum gas the spatial correlation exists because identical particles of an ideal quantum gas interact through a statistical potential which arises due to the symmetry property of the wave functions.

We assume for simplicity that the particles have no spin. We adopt the method of the second quantisation to evaluate the correlation function for a quantum gas. This method has been considered in detail in Sec.10.6.

In the second quantisation approach, the particle density operator $\hat{n}$ of the gas particles in space is given by (see Eq.(10.6.4))

$$\hat{n} = \hat{\psi}^{\dagger}(\mathbf{r})\,\hat{\psi}(\mathbf{r}) = \sum_{k,k'} \hat{a}_k^{+} \hat{a}_{k'}\, u_k^{*}(\mathbf{r}) u_{k'}(\mathbf{r}) \tag{15.9.3}$$

where $\hat{a}_k$ and $\hat{a}_k^{+}$ are, respectively, the annihilation and creation operators for the particle in the state $\mathbf{k}$ and $u_k(\mathbf{r})$ is the single-particle wave function

$$u_k(r) = (1/V^{1/2})\, e^{i\mathbf{k}.\mathbf{r}} \tag{15.9.4}$$

In (15.9.3), the summations extend over all possible value of $\mathbf{k}$ and $\mathbf{k}'$. Since the particle number operator $\hat{N}$ is

$$\hat{N} = \sum_k \hat{a}_k^{+} \hat{a}_k = \sum_k n_k \tag{15.9.5}$$

it is easy to see that

$$\sum_k \hat{a}_k^+ \hat{a}_k |u_k(r)|^2 = (1/V) \sum_k n_k = N/V = \langle n \rangle \tag{15.9.6}$$

where N is the total number of particles in the volume V, and hence N/V is the mean particle density <n> for a homogeneous gas. Thus the mean density <n> is the diagonal terms of the sum (k = k') in (15.9.3). Then (15.9.3) can be written as

$$\hat{n} = \langle n \rangle + \sum_{k,k'}{}' \hat{a}_k^+ \hat{a}_{k'} u_k^*(\mathbf{r}) u_{k'}(\mathbf{r}) \tag{15.9.7}$$

where the prime over the sum represents that the diagonal terms are omitted. $\hat{n} - \langle n \rangle$ is termed as the density fluctuation operator.

We can use this expression to calculate the mean value $\langle (n_1 - \langle n \rangle)(n_2 - \langle n \rangle) \rangle$. This is done in two steps. We first perform the quantum averaging. The result obtained in this way is then averaged in the statistical sense.

Using (15.9.7), we can write

$$(n_1 - \langle n \rangle)(n_2 - \langle n \rangle) = \sum_{k_1 k_1'} \sum_{k_2, k_2'}{}' \hat{a}_{k_1}^+ \hat{a}_{k_1} \hat{a}_{k_2}^+ \hat{a}_{k_2} u_{k_1}^*(\mathbf{r}_1) u_{k_1'}(\mathbf{r}_1) u_{k_2}^*(\mathbf{r}_2) u_{k_2'}(\mathbf{r}_2) \tag{15.9.8}$$

The summation is over all values of $\mathbf{k}_1$, $\mathbf{k}_1'$, $\mathbf{k}_2$, $\mathbf{k}_2'$. However, only those terms which contain two pairs of operators $\hat{a}_k^+ \hat{a}_k$ with the same suffix have diagonal matrix elements. Thus we obtain

$$(n_1 - \langle n \rangle)(n_2 - \langle n \rangle) = \sum_{k,k'}{}' \hat{a}_k^+ \hat{a}_k \hat{a}_{k'}^+ \hat{a}_{k'} u_k^*(\mathbf{r}_1) u_{k'}(\mathbf{r}_1) u_{k'}^*(\mathbf{r}_2) u_k(\mathbf{r}_2) \tag{15.9.9}$$

which are diagonal matrices.

Using the commutation rules for $\hat{a}_k^+, \hat{a}_{k'}$

$$[\hat{a}_{k'}, \hat{a}_k^+]_\mp = 1$$

we have

$$\hat{a}_{k'} \hat{a}_k^+ = 1 \pm \hat{a}_k^+ \hat{a}_{k'} = 1 \pm n_{k'}$$

where the upper sign refers to boson, and the lower sign to fermions. Then we obtain

$$\hat{a}_k^+ \hat{a}_{k'} \hat{a}_{k'}^+ \hat{a}_k = \hat{a}_k^+ [1 \pm \hat{a}_{k'}^+ \hat{a}_{k'}] \hat{a}_k = (1 \pm n_{k'}) n_k \tag{15.9.10}$$

Substituting this value along with (15.9.4) in (15.9.9) we obtain

$$(n_1 - \langle n \rangle)(n_2 - \langle n \rangle) = (1/V^2) \sum_{k,k'}{}' (1 \pm n_{k'}) n_k \exp[i(\mathbf{k} - \mathbf{k}').(\mathbf{r}_2 - \mathbf{r}_1)] \tag{15.9.11}$$

We now consider the statistical average of the product of the fluctuation of the particle density, which can be written as

$$<(n_1 - <n>)\,(n_2 - <n>)> \;=\; (1/V^2) \sum_{k,k'}' <(1 \pm n_{k'})n_k> \exp\,[i(\mathbf{k} - \mathbf{k}').(\mathbf{r}_2 - \mathbf{r}_1)] \qquad (15.9.12)$$

Particles belonging to different quantum states do not depend upon one another. They behave quite independently, so that

$$<(1 \pm n_{k'})n_k> \;=\; <1 \pm n_{k'}>\,<n_k> \;=\; (1 \pm <n_{k'}>)\,<n_k> \qquad (15.9.13)$$

Thus we obtain

$$<(n_1 - <n>)\,(n_2 - <n>)> \;=\; (1/V^2) \sum_{k,k'}' (1 \pm <n_{k'}>)\,<n_k> \exp\,[i(\mathbf{k} - \mathbf{k}').(\mathbf{r}_2 - \mathbf{r}_1)] \qquad (15.9.14)$$

When the volume V is large, the wave vector $\mathbf{k}$ is almost continuous, and the summation can be transferred to integration over $\mathbf{k}$, i.e.

$$(1/V) \sum_{k} \rightarrow\; (1/(2\pi)^3) \int d\mathbf{k}$$

Thus we obtain

$$<(n_1 - <n>)\,(n_2 - <n>)> = (1/(2\pi)^6) \int\int (1 \pm <n_{k'}>)\,<n_k> \exp\,[i(\mathbf{k}-\mathbf{k}').(\mathbf{r}_2-\mathbf{r}_1)]d\mathbf{k}d\mathbf{k}'$$

$$= (1/(2\pi)^6) \int\int <n_k> \exp\,[i(\mathbf{k}-\mathbf{k}').(\mathbf{r}_2-\mathbf{r}_1)]d\mathbf{k}d\mathbf{k}' \pm (1/(2\pi)^6) \int\int <n_k>\,<n_{k'}> \exp\,[i(\mathbf{k}-\mathbf{k}').(\mathbf{r}_2-\mathbf{r}_1)]d\mathbf{k}d\mathbf{k}'$$

$$= <n>\,\delta(\mathbf{r}) + <n>^2\, h(\mathbf{r}) \qquad (15.9.15)$$

where we have used the formulae

$$(1/(2\pi)^6) \int\int <n_k> \exp\,[i(\mathbf{k}-\mathbf{k}').(\mathbf{r}_2-\mathbf{r}_1)]d\mathbf{k}d\mathbf{k}' = (1/(2\pi)^3) \int <n_k> \exp\,[i\mathbf{k}.(\mathbf{r}_2-\mathbf{r}_1)]\delta(\mathbf{r}_2-\mathbf{r}_1)d\mathbf{k}$$

$$= <n>\,\delta(\mathbf{r}_2-\mathbf{r}_1) \qquad (15.9.16)$$

with

$$<n> \;=\; (1/(2\pi)^3) \int <n_k> \exp\,(i\mathbf{k}.\mathbf{r})d\mathbf{k} \qquad (15.9.17)$$

$$\delta(\mathbf{r}_2-\mathbf{r}_1) \;=\; (1/(2\pi)^3) \int \exp\,[i\mathbf{k}'.(\mathbf{r}_2-\mathbf{r}_1)d\mathbf{k}' \qquad (15.9.18)$$

and

$$h(\mathbf{r}) \;=\; \pm\,(1/<n>^2\,(2\pi)^6) \int <n_k>\,<n_{k'}> \exp\,[i(\mathbf{k}-\mathbf{k}').\mathbf{r}]d\mathbf{k}d\mathbf{k}'$$

$$= \pm\,(1/<n>^2\,(2\pi)^6)\; |\int <n_k> \exp\,[i\mathbf{k}.\mathbf{r}]d\mathbf{k}\,|^2 \qquad (15.9.19)$$

When the spin of the particles is taken into account, (15.9.19) will be modified in the form

$$h(\mathbf{r}) \;=\; \pm\,(g^2/<n>^2\,(2\pi)^6)\; |\int <n_k> \exp\,(i\mathbf{k}.\mathbf{r})d\mathbf{k}\,|^2 \qquad (15.9.20)$$

where $g = 2s + 1$, is the degeneracy due to the spin s of the particle. The plus sign holds for bosons, and the minus for fermions. The mean number of particles according to the Bose-Einstein and Fermi-Dirac statistics is

$$<n_k> \;=\; 1/(\exp((\epsilon_k - \mu)/kT) \mp 1) \qquad (15.9.21)$$

where

$$\epsilon_k = h^2k^2/2m$$

Substituting (15.9.21) in (15.9.20) and integrating over the angle parts, we obtain

$$h(r) = \pm (g^2/\langle n\rangle^2 (2\pi)^6) \| (\exp(\mathbf{k}.\mathbf{r})/(\exp((\epsilon_k - \mu)/kT) \mp 1))dk |^2$$

$$= \pm (g^2/4\pi\langle n\rangle^2 r^2) | \int_0^\infty \sin(kr)kdk/(\exp((\epsilon_k - \mu)/kT) \mp 1))|^2 \qquad (15.9.22)$$

This expression shows that $h(r)>0$ for bosons and $h(r) < 0$ for fermions. In other words, in case of bosons the particles attract each other while in case fermions they repel each other.

Let us apply the theory developed above to a degenerate Fermi gas at $T = 0$. In this case

$$\langle n_k\rangle = 1 \qquad \text{for } k < k_F$$

$$= 0 \qquad \text{for } k > k_F$$

where k_F is the Fermi wave vector corresponding to the Fermi momentum, i.e.

$$k_F = P_F/\hbar = (6\pi^2\langle n\rangle/g)^{1/3}$$

Then (15.9.22) in this case reduces to

$$h(r) = -(g^2/4\pi^2\langle n\rangle^2 r^2) | \int_0^{k_F} \sin(kr)kdk|^2 = -(g^2/4\pi^2\langle n\rangle^2 r^4) [\cos(k_Fr) - (k_Fr)^{-1} \sin(k_Fr)]^2$$

$$= -(3/2\pi^2\langle n\rangle^2 r^4) [\cos(k_Fr) - (k_Fr)^{-1} \sin(k_Fr)]^2 \qquad (15.9.23)$$

In case of $K_Fr >> 1$, we obtain from (15.9.23)

$$h(r) = -(3/2\pi^2 K_F r^4) \cos^2(k_Fr) \qquad (15.9.24)$$

Taking the average of $\cos^2(k_Fr)$, this gives

$$h(r) = -3/4\pi^2 K_F r^4 \qquad (15.9.25)$$

i.e.

$$h(r) \propto 1/r^4 \qquad (15.9.26)$$

Thus the correlation function h(r) decreases inversely as the fourth power of the distance.

In the limit $r \to 0$, the expression (15.9.20) for h(r) reduces to

$$h(r) = \pm (g^2/\langle n\rangle^2 (2\pi)^6) | \int \langle n_k\rangle \, dk|^2 = \pm 1 \qquad (15.9.27)$$

since.

$$\langle n\rangle = (g/(2\pi)^3) \int \langle n_k\rangle \, dk \qquad (15.9.28)$$

In the Boltzmann limit

$$\langle n_k \rangle = 1/(\exp((\epsilon_K - \mu)/kT) \pm 1) \qquad \exp((\epsilon_K - \mu)/kT)$$

and the correlation function is expressed in the form

$$h(r) = \pm (g^2/4\pi^2 \langle n \rangle^2 r^2)\, e^{2\mu/kT} \left| \int_0^\infty \exp(-\hbar^2 K^2)/2mkT)\, \sin(Kr)\, K\, dK \right|^2$$

$$= \pm (g^2 e^{2\mu/kT}/4\pi^3 \langle n \rangle^2)\, (2mkT/\hbar^2)^3 \exp\left[-(4mkT/\hbar^2) r^2\right] \qquad (15.9.29)$$

This gives in the classical limit ($\hbar \to 0$)

$$h(r) \to 0 \quad \text{for} \quad \hbar \to 0.$$

Thus in the classical limit, the correlation function h(r) tends to zero in accordance with the discussions given at the beginning of this section.

Problems

15.1 A circuit consists of a resistance R and a self-inductance L. In the presence of an electromotive force E in the circuit, the current, J satisfies the equation
$L\dot{J}(t) + RJ(t) = E$
Show that the time correlation function for current J is
$C_J(t) = \langle J(t)J(0) \rangle = (kT/L) \exp(-(R/L)t)$

15.2 A function changes randomly every τ_c second, but is constant otherwise. Show that the correlation function for $|\tau| \le \tau_c$ is
$C(\tau) = \langle f^2(t) \rangle [1 - |\tau|/\tau_c]$

15.3 A particle satisfies the linear equation of motion
$m\ddot{q}(t) + \gamma \dot{q}(t) = \alpha$
where q(t) is the coordinate of a particle of mass m, and γ is the frictional constant. Solve this equation with initial condition $q(0) = q_0$ and $\dot{q}(0) = 0$. Using this solution, show that the mean square fluctuation displacement of the particle is
$\langle (q(t) - q(0))^2 \rangle = (2kT/\gamma)\, (1 + (m/\gamma)\, [\exp(-\gamma t/m) - 1])$

15.4 Calculate the mean square charge of a condenser of capacity C closed across a resistance R.

15.5 Show that the mean square fluctuation of the energy is
$\langle (\Delta U)^2 \rangle = kT^2 C_v + kT[T(\partial P/\partial T)_v - P]^2\, (\partial V/\partial P)_T$

15.6 Set up the diffusion equation and solve it. Show that
$\langle r^2(t) \rangle = 6Dt$
where D is the diffusion coefficient of the system.

15.7 A Brownian particle satisfies a linear equation of motion
$d^2x(t)/dt^2 = -\tau^{-1}(dx(t)/dt) + A(t)$
Show that
$\langle x^2 \rangle = (2k\tau^2/m)[(t/\tau) - (1 - \exp(-t/\tau))]$

Discuss the limiting conditions for $\langle x^2 \rangle$

15.8 A spherical particle of radius a is moving in a fluid of coefficient of viscosity η. Show that the mean square displacement of the particle is
$\langle x^2 \rangle = (kT/3\pi a\eta)\,[t - (m/6\pi a\eta)\,(1 - \exp\{-(6\pi a\eta/m)t\})]$

15.9 Show that for an ideal Boltzmann gas, the correlation function h(r) is given by
$h(r) = \pm (g^2/4\pi^2 \langle n \rangle^2)\, e(2\mu/kT)\, (2mkT/\hbar^2)^3 \exp[-(4mkT/\hbar^2)r^2]$
Discuss that h(r) tends to zero in the classical limit.

15.10 Show that for an ideal boson or fermion, the correlation function is given by
$h(r) = \pm (g^2/(2\pi)^6 \langle n \rangle^2)\, |\int (\exp(i\mathbf{k}.\mathbf{r})d\mathbf{k}/(\exp((\epsilon - \mu)/kT) \mp 1)|^2$
where $g = 2s + 1$ is the spin degeneracy.

15.11 Show that the correlation function for a degenerate Fermi gas at temperature T less than T_F is given by
$h(r) = -(3(mkT)^2/4\hbar^4 k_F^3 r^2)\, \sinh^{-2}(\pi mkTr/\hbar^2 k_F)$
Further show that, when $T \to 0$, $h(r) \propto r^{-4}$.

15.12 If the correlation function of the fluctuation is
$C(\tau) = C(0) \exp(\tau/\tau_c)$
where τ_c is the relaxation time. Show that the spectral density is
$G(\nu) = 4C(0)\tau_c/(1+(2\pi\nu\tau_c)^2)$

15.13 Find the power spectrum for a function whose correlation function is
$C(\tau) = \langle f^2(t) \rangle\, [1 - |\tau|/\tau_c]$

15.14 Show that the power spectra $G_v(\nu)$ and $G_A(\nu)$ of the random variable v(t) and A(t) of the Langevin equation are connected by the relation
$G_v(\nu) = G_A(\nu)\, (\tau_c^2/(1+(\pi\nu\tau_c)^2))$
where $G_A(\nu) = 12kT/m\tau_c$, and τ_c is the relaxation time.

15.15 Show that the mean square velocity of a Brownian particle starting at t = 0 is
$\langle v^2(t) \rangle = v^2(0) + [(kT/m) - v^2(0)]\, [1 - \exp(-2t/\tau_c)]$
where τ_c is the relaxation time.

15.16 Establish Fokker-Planck equation and solve it. Discuss how this equation leads to the state of equilibrium.

APPENDIX A

CONVERSION FACTOR

(i) **Useful relations**

1 Newton (N)	=	10^5 dynes
1 Joule(J)	=	10^7 erg
1 Calorie	=	4.184 J
	=	4.184×10^7 erg
1 electron volt (ev)	=	1.60×10^{-12} erg
	=	1.60×10^{-19} J
	=	1.1605×10^4 K
	=	23.05 kcal mol^{-1}
1 Watt (W)	=	1 kg m^2/s^3 = 1 J/s
1 pascal (Pa)	=	10 dyne/cm^2
	=	1 N/m^2
	=	10^{-5} bar
1 Atmosphere (atm)	=	1.01325 bars
	=	1.01325×10^5 N/m^2
	=	1.01325×10^6 dyne/cm^2
	=	760 mm Hg
1 angstron (A)	=	10^{-8} cm
	=	10^{10} cycle/s

(ii) Prefixes for SI Units

Fraction	Prefix	Symbol
10^{-2}	centi	c
10^{-3}	milli	m
10^{-6}	micro	μ
10^{-9}	nano	n
Multiplier	**Prefix**	**Symbol**
10^3	killo	k
10^6	mega	M
10^9	giga	G

APPENDIX B

VALUES OF PHYSICAL CONSTANTS

Constant	Symbol	Value
Velocity of light in vacuum	c	2.9979×10^{8} m/s
Molar volume	-	22.4×10^{3} cm^3-mol
Avogadro number	N_A	6.0222×10^{23} mol^{-1}
Gas constant	R	8.3144 J^0 K^{-1} mol^{-1}
Boltzmann constant (R/N_A)	k	1.3806×10^{-23} J^0 K^{-1}
Planck constant	h	6.6262×10^{-34} J s
		$\hbar(=h/2\pi)$ 1.0546×10^{-34} J s
Charge of electron	e	1.6022×10^{-19} C
Rest mass of electron	m_e	9.1095×10^{-31} kg
Rest mass of proton	m_p	1.6726×10^{-27} kg
Rest mass of Neutron	m_n	1.6750×10^{-27} kg
Charge to mass ratio for electron	e/m_e	1.7588×10^{11} C/kg
Bohr radius ($\hbar^2/m_e e^2$)	a_0	5.2918×10^{-11} m
Bohr magneton ($e\hbar/2m_e c$)	μ_B	9.2741×10^{-24} J T^{-1}
Nuclear magneton($e\hbar/2m_e c$)	μ_N	5.0510×10^{-27} j T^{-1}
Atomic mass unit	m_u	1.66006×10^{-27} kg
Stefan-Boltzmann constant	σ	5.6696×10^{-8} W/m^2 K^4

APPENDIX C

MATHEMATICAL FUNCTIONS

In this appendix we consider some mathematical functions which have been used in the text.

1. Gamma Function

The Gamma function $\Gamma(n+1)$ is defined by the equation

$$\Gamma(n+1) = \int_0^\infty e^{-x} x^n \, dx \qquad \text{(C.1)}$$

which can be integrated by parts. Thus

$$\Gamma(n+1) = n \int_0^\infty e^{-x} x^{n-1} \, dx = n\Gamma(n)$$

Hence it follows that

$$\Gamma(n+1) = n(n-1) \ldots (l+1)l\,\Gamma(l) \qquad 1 \leq l \leq 0 \qquad \text{(C.2)}$$

When n is an integer, we have

$$\Gamma(n+1) = n(n-1) \ldots 2.1 \equiv n!$$

and hence,

$$\Gamma(1) \equiv 0! = .1$$

$$\Gamma(2) \equiv 1! = 1$$

On the other hand when n is half-odd integer, let $n = l - ½$, then

$$\Gamma(l+(1/2)) \equiv (l-(1/2))! = (1-(1/2)(1-(3/2)) \ldots (3/2).(1/2)\,\pi^{1/2}$$

where we have used

$$\Gamma(1/2) \equiv (-1/2)! = \pi^{1/2}$$

One can obtain the results for fraction of integers. Thus

$$\Gamma(n+(1/4)) = (1.5.9.13...(4n-3)/4^n)\,\Gamma(1/4)$$

$$\Gamma(1/4) = 3.62561$$

$$\Gamma(n+(1/3)) = (1.4.7.10...(3n-2)/3^n)\,\Gamma(1/3)$$

$$\Gamma(1/3) = 2.67894$$

Let us consider an integral of the type

$$I_n = n \int_0^\infty \exp(-\alpha x^2) x^n \, dx \tag{C.3}$$

where α is a constant. In order to evaluate this integral, we put

$$\alpha x^2 = y$$

then (C.3) can be written as

$$I_n = (1/2\alpha^{(n+1)/2}) \int_0^\infty e^{-y} y^{(n-1)/2} \, dy = (1/2\alpha^{(n+1)/2})\,\Gamma((n+1)/2) \tag{C.4}$$

where $n > -1$. The integral I_n comes frequently in our study. We note that

$$\int_{-\infty}^{\infty} \exp(-\alpha x^2)\, x^n \, dx = \begin{cases} 0 & \text{If n is odd integer} \\ 2I_n & \text{If n is even integer} \end{cases} \tag{C.5}$$

*2. **Stirling Formula***

The Gamma function $\Gamma(n+1)$ is identical to the factorial n!, i.e

$$n! = \int_0^\infty e^{-x} x^n \, dx \tag{C.6}$$

This integral provides the means for evaluating n!. However, the numerical evaluation of n! is a complicated problem when n is large. In order to obtain an approximation, we change the variable

$$t = x/n$$

Then (C.6) gives

$$n! = n^{n+1} \int_0^\infty e^{-nt} t^n \, dt = n^{n+1} \int_0^\infty \exp[n(-t + \ln t)]dt = n^{n+1} e^{-n} \int_0^\infty \exp[n(1 - t + \ln t)]\, dt \tag{C.7}$$

which can be written in the form

$$n! = n^{n+1} e^{-n} \left[\int_0^2 \exp [n(1 - t + \ln t)]dt + \int_2^\infty \exp [-n(1-\ln t)\, dt] \right] \tag{C.8}$$

The contribution of the second integral on the right hand side is negligible for large n. This gives

$$n! = n^{n+1} e^{-n} \int_0^2 \exp [n(1 - t + \ln t)]dt \tag{C.9}$$

Let us put

$$t = 1 + \epsilon \qquad \text{where} - 1 \leq \epsilon \leq 1$$

then we obtain

$$\ln t = \ln(1+e) = \epsilon - (\epsilon^2/2) + (\epsilon^3/3) - \ldots$$

and

$$n! = n^{n+1} e^{-n} \int_{-1}^{1} \exp [n (-(\epsilon^2/2) + (\epsilon^3/3) - \ldots)]d\epsilon \tag{C.10}$$

When n is sufficiently large, the terms containing higher powers of ϵ can be neglected. Accordingly,

$$n! \approx n^{n+1} e^{-n} \int_{-1}^{1} \exp (-n\epsilon^2/2)\, d\epsilon \approx n^{n+1} e^{-n} \int_{-\infty}^{\infty} \exp (-n\epsilon^2/2)\, d\epsilon$$

$$\approx n^{n+1} e^{-n} (2/n)^{1/2} \int_0^\infty \exp(-x)\, x^{-1/2}\, dx \tag{C.11}$$

which finally gives

$$n! \approx n^{n+1} e^{-n} (2\pi/n)^{1/2} = \sqrt{(2\pi n)}\, (n/e)^n \tag{C.12}$$

or

$$\ln n! \approx n \ln n - n + (1/2) \ln n + (1/2) \ln (2\pi) \tag{C.13}$$

This is known as the Stirling formula. This can be further simplified for large n as

$$\ln n! = n \ln n - n \tag{C.14}$$

which is usually employed in statistical physics.

3. Volume of a Hypersphere

In D- dimensional space, we consider the integral

$$I = \int_{-\infty}^{\infty} \exp [-(x_1^2 + x_2^2 + \ldots + x_D^2)\, dx_1\, dx_2 \ldots dx_D = \left[\int_{-\infty}^{\infty} \exp [-x^2]\, dx \right]^D = \pi^{D/2} \tag{C.15}$$

For D- dimensional sphere of volume V_D, the surface area S_D can be written as $r^{D-1}s_D$, where s_D is the surface area of unit sphere of volume v_D.

$$I = \int_0^\infty \exp[-r^2]\, r^{D-1} s_D\, dr = s_D \int_0^\infty \exp[-r^2]\, r^{D-1}\, dr$$

where $r^2 = x_1^2 + x_2^2 + ... + x_D^2$ in D-space. This can be evaluated to give

$$I = (1/2)\, s_D\, \Gamma(D/2) \tag{C.16}$$

where $\Gamma(L)$ is the Gamma function. From Eq.(C.15) and (C.16), we have

$$s_D = 2\pi^{D/2} / \Gamma(D/2) \tag{C.17}$$

Then the volume of a D-sphere of radius R is given by

$$V_D = \int_0^R s_D\, r^{D-1}\, dr = s_D R^D / D = \pi^{D/2} R^D / \Gamma(1+D/2) \tag{C.18}$$

and the surface area of the sphere

$$S_D = DV_D / R = D\,\pi^{D/2} R^{D-1} / \Gamma(1 + (D/2)) \tag{C.19}$$

From (C.18) and (C.19), one can obtain the volume and surface area for any values of D. Thus for examples, for D = 2

$$V_2 = \pi R^2$$

$$S_2 = 2\pi R,$$

for D = 3

$$V_3 = (4\pi/3)R^3$$

$$S_3 = 4\pi R^2$$

and for D = 4

$$V_4 = (\pi^2/2)R^4$$

$$S_4 = (2\pi^2)R^3$$

APPENDIX D

USEFUL INTEGRALS

In the theory of quantum systems, we come across integrals of the type

$$I_n^{\mp}(z) = (1/\Gamma(n)) \int_0^{\infty} (x^{n-1}/(z^{-1} e^x \mp 1)) \, dx \tag{D.1}$$

In this appendix we study the behaviour or $I_n^{\mp}(z)$ over the range of parameter z.
(i) We first evaluate the integral for $0 < z < 1$. We expand the function

$$1/(z^{-1} e^x \mp 1) = z e^{-x} [1 \mp z e^{-x}]^{-1} = \sum_{l=1} (\pm 1)^{l-1} z^l e^{-lx}$$

Then $I_n^{\mp}(z)$ can be evaluated as

$$I_n^{\mp}(z) = (1/\Gamma(n)) \sum_{l=1}^{\infty} (\pm 1)^{l-1} z^l \int_0^{\infty} e^{-lx} x^{n-1} \, dx = \sum_{l=1}^{\infty} (\pm 1)^{l-1} (z^l/l^n) \tag{D.2}$$

From (D.2), we obtain

$$I_n^{-}(z) \equiv g_n(z) = \sum_{l=1}^{\infty} (z^l/l^n) \tag{D.3}$$

and

$$I_n^{+}(z) \equiv f_n(z) = \sum_{l=1}^{\infty} (-1)^{l-1} (z^l/l^n) = (1 - 2^{1-n}) \, g_n(z) \tag{D.4}$$

When $z = 1$, these functions reduce to

$$g_n(1) = \sum_{l=1}^{\infty} 1/l^n \equiv \xi(n) \tag{D.5}$$

$$f_n(1) = \sum_{l=1} (-1)^{l-1} (1/l^n) \equiv \eta(n) \tag{D.6}$$

where $\xi(n)$ is the Riemann zeta function defined as

$$\xi(n) = \sum_{l=1} 1/l^n = (1/1^n) + (1/2^n) + (1/3^n) + \ldots \tag{D.7}$$

and $\eta(n)$ is

$$\eta(n) = \sum_{l=1}^{\infty} (-1)^{l-1} (1/l^n) = (1/1^n) - (1/2^n) + (1/3^n) - (1/3^n) + \ldots = (1 - 2^{1-n})\, \xi(n) \qquad (D.8)$$

Thus we find that

$$\xi(n) = (1/\Gamma(n)) \int_0^{\infty} (x^{n-1}/(e^x - 1))\, dx \qquad (D.9)$$

and

$$\eta(n) = (1/\Gamma(n)) \int_0^{\infty} (x^{n-1}/(e^x + 1))\, dx \qquad (D.10)$$

Value of the first few zeta functions are given below

$\xi(3/2) = 2.612$ $\qquad$ $\xi(5/2) = 1.341$

$\xi(2) = \pi^2/6$ $\qquad$ $\xi(4) = \pi^4/90$

$\xi(3) = 1.202$ $\qquad$ $\xi(5) = 1.037$

(ii) Next we evaluate the integral for large values of z as in the case of Fermi system. Here we introduce a variable

$$\gamma \equiv \ln z$$

then (D.1) takes the form

$$J_n^+(\gamma) \equiv J_n^+(z) = \Gamma(n)\, I_n^+(z) = \int_0^{\infty} (x^{n-1}/(e^{x-\gamma} + 1))\, dx \qquad (D.11)$$

In order to solve (D.11), we put

$$x - \gamma = y$$

then

$$J_n^+(\gamma) = \int_{-\gamma}^{\infty} ((\gamma + y)^{n-1}/(e^y + 1))\, dy = \int_0^{\gamma} ((\gamma - y)^{n-1}/(e^{-y} + 1))\, dy + \int_0^{\infty} ((\gamma + y)^{n-1}/(e^y + 1))\, dy$$

When we use the relation

$$(1/e^{-y}+1) = 1 - (1/e^{-y}+1)$$

$J_n^+(\gamma)$ can be written as

$$J_n^+(\gamma) = \int_0^{\gamma} x^{n-1}\, dx - \int_0^{\gamma} ((\gamma - y)^{n-1}/(e^y + 1))\, dy + \int_0^{\infty} ((\gamma + y)^{n-1}/(e^y + 1))\, dy$$

$$= (1/n)\,\gamma^n + \int_0^\infty \{((\gamma + y)^{n-1} - (\gamma - y)^{n-1})/(e^y + 1)\}\,dy + \int_\gamma^\infty ((\gamma - y)^{n-1})/(e^y + 1))\,dy$$

Since $\gamma \gg 1$, the contribution of the last integral is very small, and can be neglected. After expanding

$$(\gamma \mp y)^{n-1} = \gamma^{n-1}\,(1 \mp (y/\gamma))^{n-1} = \sum_{K=1}^{n-1} (\mp 1)^k \binom{n-1}{K} \gamma^{n-1-K}\, y^K$$

$$= \gamma^{n-1}\,[1 \mp (n-1)\,(y/\gamma) + ((n-1)\,(n-2)/2!)\,(y/\gamma)^2 \mp ((n-1)\,(n-2)\,(n-3)/3!)\,(y/\gamma)^3 + \ldots$$

$$+ ((n-1)\,(n-2)\ldots(n-K)/K!)\,(y/\gamma)^K + \ldots\,]$$

we obtain

$$J_n^+(\gamma) = (1/n)\,\gamma^n + \int_0^\infty \{((\gamma + y)^{n-1} - (\gamma - y)^{n-1})/(e^y + 1)\}\,dy$$

$$= (1/n)\,\gamma^n + 2 \sum_{K=1,3,5,\ldots} \binom{n-1}{K} \gamma^{n-1-K}\, I_{K+1}^+(1) \qquad \text{(D.12)}$$

where

$$I_{K+1}^+(1) = (1/\Gamma(K+1)) \int_0^\infty (y^K/(e^y + 1))\,dy = 1 - (1/2^{K+1}) + (1/3^{K+1}) - (1/4^{K+1}) + \ldots \qquad \text{(D.13)}$$

Substituting (D.13) in (D.12), finally we obtain

$$J_n^+(\gamma) = (\gamma^n/n)\,[1 + 2 \sum_{K=2,4,6,\ldots} n\,(n-1)\,(n-2)\ldots(n-K+1)\,(I_K^+(1)/\gamma^K)] \qquad \text{(D.14)}$$

This is the asymptotic result for the Fermi-Dirac system. Thus we obtain

$$f_n(z) = J_n^+(\gamma)/\Gamma(n)$$

$$= (\gamma^n/\Gamma(n+1))\,[1 + (n(n-1)/6)\,(\pi/\gamma)^2 + (7n\,(n-1)\,(n-2)\,(n-3)/360)\,(\pi/\gamma)^4 + \ldots\,] \qquad \text{(D.15)}$$

APPENDIX E

PROBABILITY DISTRIBUTION FUNCTIONS

In this appendix, we discuss the properties of the probability density. To begin with, we consider a system of N noninteracting identical particles enclosed in a container of volume V. For noninteracting systems the probability density $\rho(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$ of the system in space is

$$\rho(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) = \prod_{i=1}^{N} \rho(\mathbf{r}_i) \tag{E.1}$$

where $\rho(\mathbf{r}_i)$ is the probability density that the ith particle is located at the point $\mathbf{r}_i$.

Let us find out the probability that n particles are located in the volume v and the remaining (N-n) occupy the volume (V-v) of the container. The number of different ways of choosing n particles from a total number of particles N is

$$C_N^n = N!/n!(N-n)! \tag{E.2}$$

Let P(v) be the probability of finding a particle in the volume v while $q(v) \equiv 1 - P(v)$ is the probability of finding the particle in the remaining volume V – v, then

$$P(v) = \int_v \rho(\mathbf{r})\, d\mathbf{r}$$

$$q(v) = 1 - P(v) = \int_{V-v} \rho(\mathbf{r})\, d\mathbf{r} \tag{E.3}$$

such that

$$P + q = 1$$

since the particle is either in the volume v or V-v. Since the particles are noninteracting, the probability of finding n particles within the volume v and remaining N – n particles within the volume V – v is given by

$$P^n(v)\, q^{N-n}(v) = P^n(v)\, [1 - P(v)]^{N-n} \tag{E.4}$$

This is only the number of distinct particles corresponding to a certain definite set of particles n in the volume v. However, (E.2) gives the number of different ways in which n particles can be selected from N particles. Hence the probability of finding n arbitrary chosen particles in the volume v is given by

$$\rho_N(n) = (N!/n!(N-n)!)\, P^n[1-P]^{N-n} \tag{E.5}$$

This is known as binomial distribution, which satisfies the normalisation condition

$$\sum_{i=1}^{N} \rho_N(n) = 1 \tag{E.6}$$

It can be seen that for $n = 0$ and for $n \to N$, $\rho_N(n)$ is very small, i.e.

$$\rho_N(n \to 0) \quad q^N \to 0$$

$$\rho_N(n \to N) \quad P^N \to 0$$

For certain intermediate values of n, $\rho_N(n)$ attains its maximum value, where

$$d\rho_N(n)/dn = 0 \tag{E.7}$$

Using Stirling formula, (E.2) can be written as

$$N!/n!(N-n)! \quad (N/e)^N / [(n/e)^n (N-n)/e]^{N-n} \quad (N/n)^n \{ (N/e)^{N-n}/(N/n)^{N-n} (1-(n/N))^{N-n}\}$$

$$(N/n)^n \{(1-(n/N)^n)/(1-(n/N)^N)\} \tag{E.8}$$

Since $N \to \infty$, $(1-(n/N))^N = e^{-n}$. Then

$$N!/n!(N-n)! \quad (Ne/n)^n (1-(n/N)^n) \quad (Ne/n)^n \tag{E.9}$$

and (E.5) takes the form

$$\rho_N(n) \quad (Ne/n)^n P^n q^{N-n} \quad (NeP/nq)^n q^N \tag{E.10}$$

or

$$\ln \rho_N(n) = n \ln(NeP/nq) + N \ln q \tag{E.11}$$

We consider the case when N is large and q 1. Differentiating this expression with respect to n, and putting it equal to zero, we obtain the value of n for the maximum probability:

$$\ln (NeP/nq) - 1 = 0$$

or

$$n \quad NP/q \quad NP \tag{E.12}$$

since q = 1. This relation is accurate for a large number N of the particles in the volume V when v is not too small. It is clear from this result that $\rho_{max} = n/v$ is the most probable density in volume v, while $\rho_0 = N/V$ is the density of the particles in the entire volume V as if the particles are uniformly distributed over the entire volume. If P = v/V, (E.12) leads to

$$\rho_{max} = \rho_0 \tag{E.13}$$

Thus we conclude that the most probable distribution of the particle density in volume v is the uniform distribution over the entire volume.

Let us consider two important limiting cases:

1. The Poisson distribution

Let $\langle n \rangle$ be the mean number of particles in the volume v. Since N/V is the mean number of particles over the entire volume,

$$\langle n \rangle / v = N/V$$

or

$$P = v/V = \langle n \rangle / N \tag{E.14}$$

Substituting this value in (E.5), we get

$$\begin{aligned} \rho_N(n) &= (N!/n!(N-n)!)\,(\langle n \rangle/N)^n\,(1-(\langle n \rangle/N))^{N-n} \\ &= (N(N-1)\ldots(N-n+1)/n!)\,(\langle n \rangle)^n/N^n)\,(1-(\langle n \rangle/N))^{N-n} \\ &= 1(1-(1/N))\,(1-(2/N))\ldots(1-((n-1)/N))\,((\langle n \rangle)^n/n!)\,(1-\langle n \rangle/N)^N)/(1-\langle n \rangle/N)^n \end{aligned} \tag{E.15}$$

In the limit $N \to \infty$,

$$(1-\langle n \rangle/N)^N = \exp(-\langle n \rangle)$$

and (E.15) reduces to

$$\rho_N(n) = \lim_{N \to \infty} \rho_N(n) = ((\langle n \rangle)^n/n!)\exp(-\langle n \rangle) \tag{E.16}$$

(E.16) is called the Poisson distribution. It is easily seen to satisfy the normalisation condition

$$\sum_{i=1}^{\infty} \rho_N(n) = 1 \tag{E.17}$$

with the help of this distribution we can calculate the mean square of the number of particles

$$\begin{aligned} \langle n^2 \rangle &= \sum_{n=0}^{\infty} n^2\,\rho(n) = \exp(-\langle n \rangle) \sum_{n=0}^{\infty} n^2(\langle n \rangle)^n/n! = \exp(-\langle n \rangle) \sum_{n=0}^{\infty} n(\langle n \rangle)^n/(n-1)! \\ &= \langle n^2 \rangle \sum_{n=0}^{\infty} \exp(-\langle n \rangle)\,(\langle n \rangle)^{n-2}/(n-2)! + \langle n \rangle \sum_{n=0}^{\infty} \exp(-\langle n \rangle)\,(\langle n \rangle)^{n-1}/(n-1)! \\ &= \langle n^2 \rangle + \langle n \rangle \end{aligned} \tag{E.18}$$

Hence the mean square of the number of particles is

$$\langle (\Delta n)^2 \rangle = \langle n^2 \rangle - \langle n \rangle^2 = \langle n \rangle \tag{E.19}$$

2. Gauss distribution

Let us consider the case when $\langle n \rangle \gg 1$ and $\Delta n = n - \langle n \rangle \ll \langle n \rangle$. Taking the lograthim of the Poisson distribution, we get

$$\ln \rho(n) = n \ln n_0 - n_0 - \ln n!,$$

where $n_0 \equiv \langle n \rangle$. Using Stirling's formula $\ln n! = n \ln n - n$ for $n \gg 1$, we obtain

$$\ln \rho(n) = n \ln n_0 - n_0 - n \ln n + n = n \ln [1 + (n_0 - n)/n] - (n_0 - n)$$

$$-(1/2)\,(n_0 - n)^2/n \qquad - (n - n_0)^2/2n_0 \tag{E.20}$$

or

$$\rho(n) = A \exp [- (n - n_0)^2/2n_0] \tag{E.21}$$

where A is a normalisation constant, which can be determined using the normalisation condition,

$$\sum_n \rho(n) = 1 \tag{E.22}$$

When $n \gg 1$, we may regard n as a continuous variable, which may extend to the whole interval $-\infty < n < \infty$. Then from the normalisation condition

$$\int_{-\infty}^{\infty} \rho(n)\, dn = 1 \tag{E.23}$$

we get

$$A \int_{-\infty}^{\infty} \exp (- (n - n_0)^2/2n_0) dn = 2A \int_0^{\infty} \exp (- (n - n_0)^2/2n_0) dn$$

$$= \sqrt{2n_0}\, A \int_0^{\infty} e^{-y}\, y^{-1/2}\, dy = \sqrt{2\pi n_0}\, A$$

or

$$A = 1/\sqrt{2\pi n_0}$$

Thus the probability density distribution can be written in the form

$$\rho(n) = (1/\sqrt{2\pi n_0}\,) \exp [- (n - n_0)^2/2n_0] \tag{E.24}$$

This is the Gaussian distribution (or the normal distribution). We have shown that

$$\langle (\Delta n)^2 \rangle = \langle (n - n_0)^2 \rangle = n_0$$

which is true for this distribution also. Let $\sigma_0 = \sqrt{\langle (\Delta n)^2 \rangle}$; then the Gaussian distribution can be expressed in the standard form

$$\rho(x) = (1/\sigma_0\sqrt{2\pi}) \exp [- (x - x_0)^2/2\sigma_0^2] \qquad -\infty < x < \infty \tag{E.25}$$

which satisfies the normalisation condition

$$\int_{-\infty}^{\infty} \rho(x)\, dx = 1$$

where x_0 is the mean value of the variable x, while σ_0 represents its root mean square fluctuation from the mean value. Figure E.1 shows this distribution for different values of σ_0. The smaller the root mean square fluctuation σ_0, the higher and narrower is the maximum.

3. Error function

The errors of measurements are assumed to be random ones, and governed by the Gaussian distribution. The probability that the error in the measurement of the quantity x lies between the limits ±a is given by

$$P(a) = (1/\sigma_0\sqrt{2\pi}) \int_{-a}^{a} \exp\left[-(x - x_0)^2/2\sigma_0^2\right] dx$$

$$= (2/\sigma_0\sqrt{2\pi}) \int_{0}^{a} \exp\left[-(x - x_0)^2/2\sigma_0^2\right] dx \qquad \text{(E.26)}$$

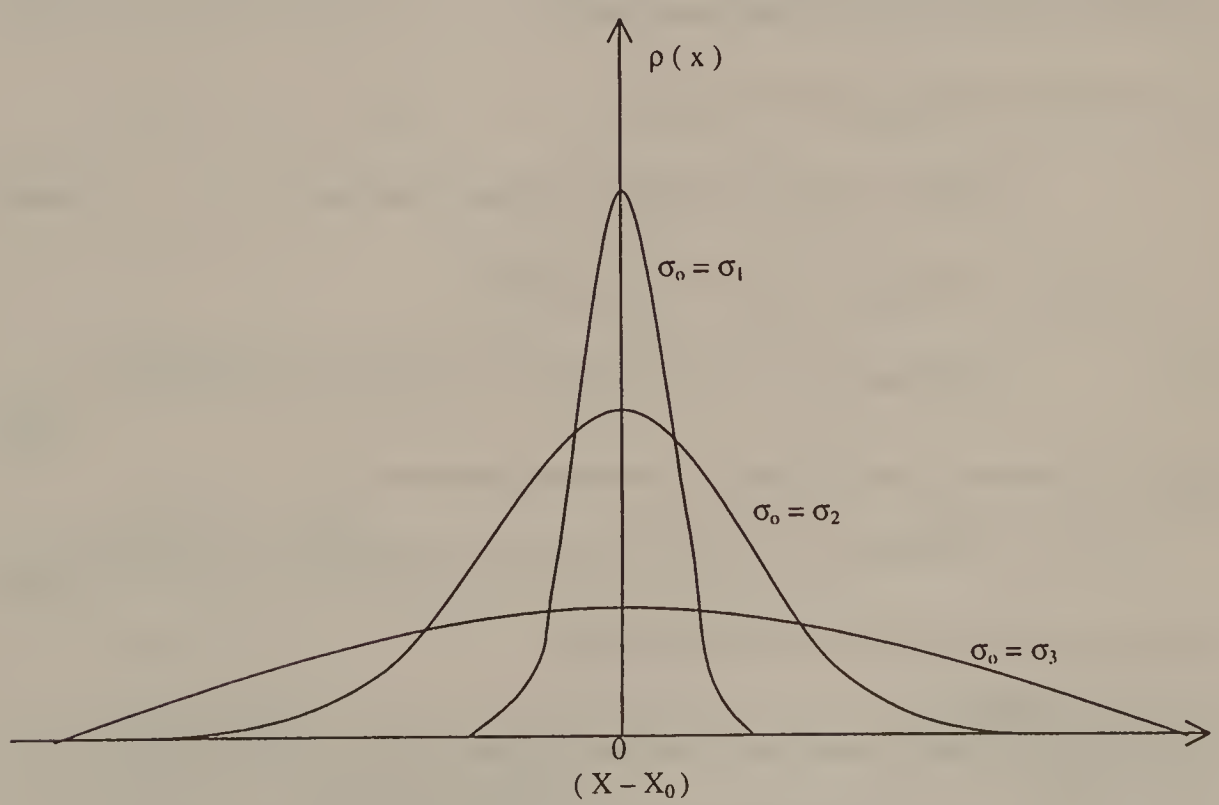


Fig.E.1. The Gaussian distribution for different values of $\sigma_0(\sigma_1<\sigma_2<\sigma_3)$

Putting $(x - x_0)^2/2\sigma_0^2 = t^2$, we can write

$$P(a) = (2/\sqrt{\pi}) \int_0^{a/\sqrt{2}\sigma_o} \exp(-t^2)\, dt = \text{erf}\,(a/\sqrt{2}\sigma_o) \tag{E.27}$$

This integral is known as the error function. Thus the error function is defined as

$$\text{erf}(x) = (2/\sqrt{\pi}) \int_0^x \exp(-t^2)\, dt \tag{E.28}$$

and the complementary error function

$$\text{erfc}\,(x) = (2/\sqrt{\pi}) \int_x^\infty \exp(-t^2)\, dt = 1 - \text{erf}(x) \tag{E.29}$$

It is obvious that

$$\text{erf}(0) = 0$$

and

$$\text{erf}\,(\infty) = 1$$

A few series expansions for the error function are given by

$$\text{erf}\,(x) = (2/\sqrt{\pi}) \sum_{n=0}^{\infty} (-1)^n x^{2n+1} / (2n + 1)\, n!$$

$$= (2/\sqrt{\pi}) [x - (x^3/3.1!) + (x^5/5.2!) - (x^7/7.3!) + (x^9/9.4!) - \ \ldots\ ] \tag{E.30}$$

$$\text{erf}\,(x) = (2/\sqrt{\pi}) \exp(-x^2) \sum_{n=0}^{\infty} (2^n / 1.3 \ldots (2n+1)) x^{2n+1}$$

$$= (2/\sqrt{\pi}) \exp(-x^2) [x + (2x^3/1.3) + (4x^5/1.3.5) + (8x^7/1.3.5.7) + (16x^9/1.3.5.7.9) + \ \ldots\ ] \tag{E.31}$$

These two expressions are useful for small x. It can also be expressed as

$$\text{erfc}\,(x) = (2/\sqrt{\pi x}) \exp(-x^2) [1 - (1/2x^2) + (1.3/(2x^2)^2) - (1.3.5/(2x^2)^3) + (1.3.5.7/(2x^2)^4) - \ldots\ ] \tag{E.32}$$

It is expected to provide a good approximation for large x.

4. The Dirac δ-function

The Dirac δ- function was first introduced in quantum mechanics by Dirac. It has wide applications in statistical physics.

Let us consider the Gaussian distribution function viz.(E.25), in the limit $\sigma_o \to 0$, where the function has the following values

$$\lim_{\sigma_0 \to \infty} P(x - x_0) = \lim_{\sigma_0 \to \infty} (1/\sigma_0\sqrt{2\pi}) \exp [-(x - x_0)^2/2\sigma_0^2]$$

$$= \infty \qquad \text{when } x = x_0$$

$$= 0 \qquad \text{when } x \neq 0$$

This limiting form of the function $P(x - x_0)$ is called the Dirac δ- function. It is defined as

$$\delta(x - x_0) = \lim_{\sigma_0 \to \infty} (1/\sigma_0\sqrt{2\pi}) \exp [-(x - x_0)^2/2\sigma_0^2] \tag{E.33}$$

which satisfies the following relations

$$\delta(x - x_0) = 0 \qquad \text{for } x \neq x_0$$

$$= \infty \qquad \text{for } x = x_0 \tag{E.34a}$$

while

$$\int_{-\infty}^{\infty} \delta(x - x_0)dx = 1 \tag{E.34b}$$

We can take any range as limits of integration such that $x = x_0$ lies between them. If $f(x)$ is any continuous function of x, we have

$$\int_{-\infty}^{\infty} f(x)\, \delta(x - x_0)\, dx = f(x_0) \tag{E.35}$$

By making a change of origin, we can have

$$\delta(x) = 0 \qquad \text{for } x \neq 0$$

$$\int_{-\infty}^{\infty} \delta(x)\, dx = 1 \tag{E.36}$$

and

$$\int f(x)\, \delta(x)\, dx = f(0) \tag{E.37}$$

It has some specific properties. They are

$$\delta(x) = \delta(-x)$$

$$\delta(\alpha x) = \alpha^{-1}\, \delta(x)$$

$$\delta(x^2 - \alpha^2) = (2\alpha)^{-1} [\delta(x+\alpha) + \delta(x-\alpha)]$$

$$\int \delta(x-\alpha)\, \delta(x-\beta)dx = \delta(\alpha - \beta) \tag{E.38}$$

There are other process which are frequently used to represent the δ- function. For example, the δ-function is defined as the Fourier transform of a constant, i.e

$$\delta(x - x_0) = (1/2\pi) \int_{-\infty}^{\infty} \exp [ik(x - x_0)]\, dk \tag{E.39}$$

This definition of the δ- function can be easily extended to three dimensions

$$\delta(\mathbf{r}) = (1/(2\pi)^3) \int \exp (i\mathbf{k}.\mathbf{r})\, d\mathbf{k} \tag{E.40}$$

such that

$$\delta(\mathbf{r}) = 0 \qquad \text{if } r \neq 0 \tag{E.41}$$

and

$$\int \delta(\mathbf{r})\, d\mathbf{r} = 1$$

It can be expressed as

$$\delta(\mathbf{r}) = \delta(x)\, \delta(y)\, \delta(z) \tag{E.42}$$

Another representation of the δ- function is

$$\delta(x) = \lim_{a \to \infty} (\sin ax/\pi x) \tag{E.43}$$

The δ- function can be obtained from the differentiation of a step function $\in (x - x_0)$ defined as

$$\begin{aligned} \in (x - x_0) &= 0 \qquad \text{for } x < x_0 \\ &= 1 \qquad \text{for } x > x_0 \end{aligned} \tag{E.44}$$

which shows that

$$\delta(x - x_0) = (d/dx) \in (x - x_0) = \in'(x - x_0) \tag{E.45}$$

APPENDIX F

PATH INTEGRAL FORMULATION OF STATISTICAL MECHANICS

The Feynman path integral approach can be used to derive a formulation of statistical mechanics. In this formulation one begins with the density matrix ρ, which satisfies the equation

$$\partial\rho/\partial\beta = -\hat{H}\rho \tag{F.1}$$

where $\hat{H}$ is the Hamiltonian of the system. For simlicity, we consider a one-dimensional system. In the coordinate representation, the density matrix can be written as

$$\rho(x, x', \beta) = \langle x|\exp(-\beta\hat{H})|x'\rangle \tag{F.2}$$

The diagonal element $\rho(x, x)$ represents the probability of finding the particle at x. Hence the quantum mechanical partition function is given by

$$Q = \int dx\, \rho(x, x) = \int dx\, \langle x|\exp(-\beta\hat{H})|x'\rangle \tag{F.3}$$

We define a new quantity $t = -\beta\hbar$ which has the dimension of time. Then (F.1) can be rewritten as

$$\hbar(\partial\rho/\partial t) = -\hat{H}\rho \tag{F.4}$$

which has the formal solution

$$\rho(t) = \exp(-\hat{H}\, t/\hbar) \tag{F.5}$$

We divide the time interval (0,t) into p equal parts, each of length $\epsilon = t/p$, so that

$$\rho(t) = \exp(-\hat{H}\epsilon/\hbar)\exp(-\hat{H}\epsilon/\hbar)\ldots\exp(-\hat{H}\epsilon/\hbar) = \rho(\epsilon)\,\rho(\epsilon)\ldots\rho(\epsilon) \tag{F.6}$$

which contains p factors. In the coordinate representation, the density matrix $\rho(x, x', t)$ can be expressed as

$$\rho(x, x', t) = \langle x|\exp(-\hat{H}\, t/\hbar)|x'\rangle$$

$$= \int\ldots\int dx_1\, dx_2 \ldots dx_{p-1} \langle x|\exp(-\hat{H}\epsilon/h)|x_1\rangle\langle x_1|\exp(-\hat{H}\epsilon/h)|x_2\rangle\ldots\langle x_{p-1}|\exp(-\hat{H}\epsilon/\hbar)|x'\rangle$$

$$= \int\ldots\int dx_1\, dx_2 \ldots dx_{p-1}\ \rho(x, x_1, \epsilon)\,\rho(x_1, x_2, \epsilon)\ldots\rho(x_{p-1}, x', \epsilon) \qquad \text{(F.7)}$$

where use has been made of the closure relation

$$\int dx_i\, |x_i\rangle\langle x_i| = 1 \qquad \text{(F.8)}$$

The particle moves from x to x' through a series of intermediate steps $x_1, x_2, \ldots x_{p-1}$ as shown in Fig. F.1, in a time t. As $P \to \infty$, $\epsilon \to 0$, and the number of integrations on the intermediate variables becomes infinite. In this case, we write symbolically

$$\Phi[x(t)] = \lim_{\substack{\epsilon \to 0 \\ p \to \infty}} \rho(x, x_1, \epsilon)\,\rho(x_1, x_2, \epsilon) \ldots \rho(x_{p-1}, x, \epsilon) \qquad \text{(F.9)}$$

and

$$x(t) = \lim_{p \to \infty} dx_1\, dx_2 \ldots dx_{p-1} \qquad \text{(F.10)}$$

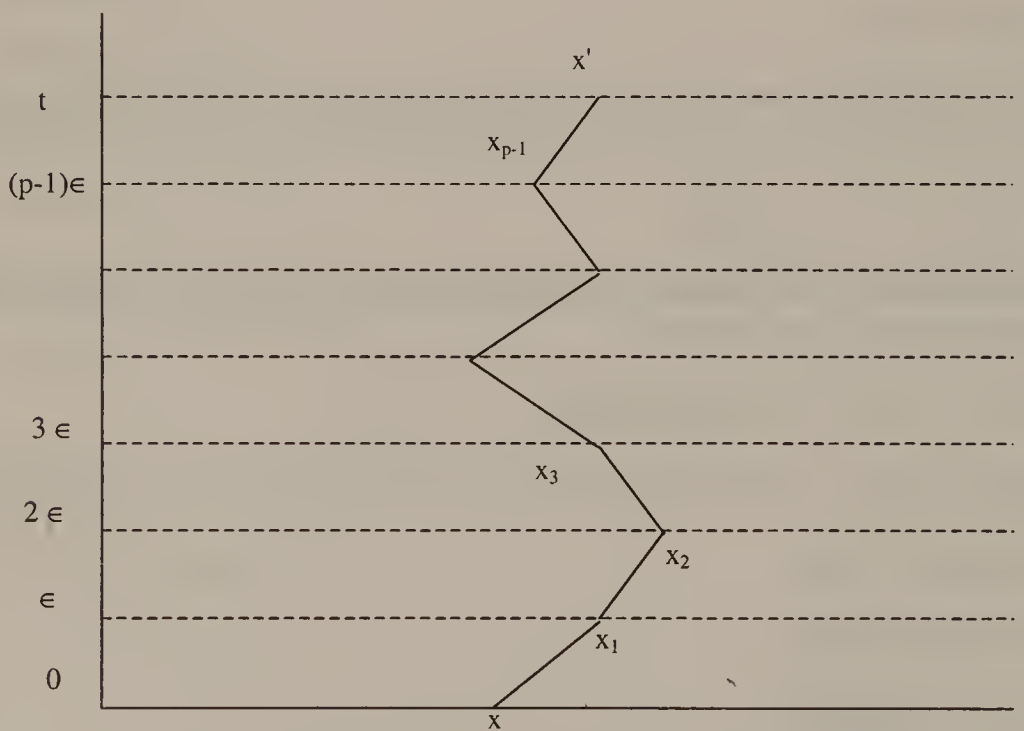


Fig.F.1. A particle moving from x to x' along $x_1\, x_2 \ldots x_{p-1}$

Then (F.7) can be written as

$$\rho(x, x', t) = \int\!\!\!\int \Phi[x(t)]\quad x(t) \qquad \text{(F.11)}$$

All possible paths are considered in (F.11). However, the main contribution comes only from those paths for which $\rho(x_1, x_2, \epsilon)$ is not negligibly small.

Let us calculate Φ for a particle moving freely in one-dimension. The Hamiltonian for such a particle is

$$\hat{H} = -(\hbar^2/2m)(\partial^2/\partial x^2) \tag{F.12}$$

The differential equation for ρ becomes

$$-\hbar(\partial\rho/\partial t) = -(\hbar^2/2m)(\partial^2\rho/\partial x^2) \tag{F.13}$$

In an infinitesimal time interval ϵ, the particle may be assumed as moving freely. We solve this equation for each interval ϵ. Thus we obtain

$$\rho(x, x', \beta/p) = (mp/2\pi\hbar^2\beta)^{1/2} \exp[(mp/2\hbar^2\beta)(x - x')^2] \tag{F.14}$$

or

$$\rho(x, x', \epsilon) = (m/2\pi\hbar\epsilon) \exp[-(m/2\hbar\epsilon)(x - x')^2] \tag{F.15}$$

Substituting (F.14) into (F.9), we obtain

$$\rho(x, x', \hbar\beta) = \lim_{\epsilon \to \infty} \int \ldots \int \exp\{-(m\epsilon/2\hbar)[((x-x_1)/\epsilon)^2 + ((x_1-x_2)/\epsilon)^2 + \ldots + ((x_{p-1}-x')/\epsilon)^2]\} \prod_{i=1}^{p-1} (dx_i/\sqrt{(2\pi\hbar\epsilon/m)}) \tag{F.16}$$

In case of an infinitesimal small time ϵ,

$$(x_i - x_{i+1})/\epsilon = [dx(t)/dt]_{t=i\epsilon} \equiv [\dot{x}(t)]_{t=i\epsilon}$$

Then for a free particle,

$$\Phi[x(t)] = \lim_{\epsilon \to \infty} \exp\{-(m\epsilon/2\hbar)[((x-x_1)/\epsilon)^2 + ((x_1-x_2)/\epsilon)^2 + \ldots + ((x_{p-1} - x')/\epsilon)^2]\}$$

$$= \exp\{-(1/\hbar)\int_0^{\hbar\beta} (m/2)[\dot{x}(t)]^2 dt\} \tag{F.17}$$

and

$$x(t) = \lim_{\epsilon \to \infty} \prod_{i=1}^{p-1} (dx_i/\sqrt{(2\pi\hbar\epsilon/m)}) \tag{F.18}$$

Thus for a free particle, $\rho(x, x', \hbar\beta)$ is

$$\rho(x, x', \hbar\beta) = \int\!\!\!\int x(t) \exp\{-(1/\hbar)\int_0^{\hbar} (1/2)m[\dot{x}(t)]^2 dt\} \tag{F.19}$$

and hence the quantum mechanical partition function is given by

$$Q = \int dx \int\!\!\!\int x(t) \exp\{-(1/\hbar)\int_0^{\hbar\beta} (1/2)m[\dot{x}(t)]^2 dt\} \tag{F.20}$$

where x(t) implies that the paths are constrained to begin and end at the point x.

In the classical limit, the temperature is high and $\hbar\beta$ is small. Then (F.19) reduces to

$$\rho_c(x, x', \hbar\beta) = (m/2\pi\hbar^2\beta)^{1/2} \exp [-(m/2\hbar^2\beta)(x - x')^2] \tag{F.21}$$

and the classical partition function is

$$Q_c = \int \rho_c(x, x, \hbar\beta)\, dx \tag{F.22}$$

For a linear system of length L, (F.22) leads to

$$Q_c = \int_0^L \rho_c(x, x, \hbar\beta)\, dx = (mkT/2\pi\hbar^2)^{1/2} L \tag{F.23}$$

From this equation the free energy of the system is

$$A = -kT \ln Q = -(1/2)\, kT \ln (mkT/2\pi\hbar^2) - kT \ln L \tag{F.24}$$

We now consider a particle moving in one-dimension under the influence of potential u(x). The Hamiltonian in this case is

$$H = -(\hbar^2/2m)(\partial^2/\partial x^2) + u(x) \tag{F.25}$$

The differential equation of ρ is

$$-\hbar (\partial\rho/\partial t) = -(\hbar^2/2m)(\partial^2\rho/\partial x^2) + u(x)\, \rho \tag{F.26}$$

In an infinitesimal time interval ϵ, the particle may be assumed as moving freely, and the presence of potential u(x) has a minor effect producing a small correction. We can write

$$\rho = \rho_0 + \delta\rho \tag{F.27}$$

where ρ_0 is ρ for free particle and $\delta\rho$ is a correction due to the presence of potential u(x). When ϵ is small, $|x - x'|$ is also small, and u(x) is constant over the range of integration. To a good approximation we can write

$$\delta\rho(x, x', \epsilon) = -(\epsilon/\hbar)\, u(x)\, \rho_0(x, x', \epsilon) \tag{F.28}$$

and hence

$$\rho(\epsilon) \approx \rho_0(\epsilon)\, [1 - (\epsilon/\hbar)\, u(x)] \qquad \rho_0(\epsilon) \exp [-u(x)\epsilon/\hbar] \tag{F.29}$$

So we obtain an expression for $\rho(x, x', \epsilon)$ in the presence of potential

$$\rho_0(x, x', \epsilon) \approx (m/2\pi\hbar^2\epsilon)^{1/2} \exp - [(m(x-x')^2/2\hbar\epsilon) + (\epsilon\, u(x)/\hbar)] \tag{F.30}$$

This is true for each element of the path of the particle. Substituting this value in (F.9), we obtain

$$\rho(x, x', \hbar\beta) = \int\!\!\int \exp\{-(1/\hbar)\int_0^{\hbar\beta} [(1/2)m\dot{x}^2(t) + u[x(t)]\,]dt\}\; x(t)$$

$$= \int\!\!\int \Phi[x(t)]\; x(t) \qquad \text{(F.31)}$$

where

$$\Phi[x(t)] = \exp\{-(1/\hbar)\int_0^{\hbar\beta} [(1/2)m\dot{x}^2(t) + u[x(t)]\,]dt\} \qquad \text{(F.32)}$$

So the partition function in this case is

$$Q = \int dx\, [\int\!\!\int x(t) \exp\{-(1/\hbar)\int_0^{\hbar\beta} [(1/2)m\dot{x}^2(t) + u[x(t)]\,]dt\}] \qquad \text{(F.33)}$$

This can be written in the form

$$Q = \int dx\, [\int\!\!\int x(t) \exp\{-(1/\hbar)\int_0^{\hbar\beta} (1/2)m\dot{x}^2(t)\, dt\}] < \exp\{-(1/\hbar)\int_0^{\hbar\beta} u[x(t)]dt\} > dt \qquad \text{(F.34)}$$

where <...> denotes a statistical average.

In the classical limit, we assume that u(x(t)) u(x), then

$$< \exp\{-(1/\hbar)\int_0^{\hbar\beta} u[x(t)]dt\} > \quad <\exp\{-(u(x)/\hbar)\int_0^{\hbar\beta} dt\}> \quad \exp\{-\beta u(x)\} \qquad \text{(F.35)}$$

and (F.31) can be written as

$$\rho(x, x', \hbar\beta) \quad \exp[-\beta u(x)] \int\!\!\int \exp[-(1/\hbar)\int_0^{\hbar\beta} (1/2)m\dot{x}^2(t)\, dt] \; x(t)$$

$$\exp[-\beta u(x)]\, \rho_0(x, x', \hbar\beta)$$

$$(m/2\pi\hbar^2\beta)^{1/2} \exp[-(m(x-x')^2/2\hbar^2\beta) - \beta u(x)] \qquad \text{(F.36)}$$

Then the classical partition function is given as

$$Q_c = \int_{-\infty}^{\infty} d(x)\, \rho(x, x, \hbar\beta) = (m/2\pi\hbar^2\beta)^{1/2} \int_{-\infty}^{\infty} \exp[-\beta u(x)]\, dx \qquad \text{(F.37)}$$

If we identify the average in (F.32) as an effective Boltzmann factor

$$\exp[-\beta U^c(x)] = <\exp\{-(1/\hbar)\int_0^{\hbar\beta} u[x(t)]\, dt\}> \qquad \text{(F.38)}$$

then the partition function attains the classical form

$$Q = (m/2\pi\hbar^2\beta)^{1/2} \int_0^{\hbar\beta} \exp[-\beta U^c(x)]\, dt \qquad \text{(F.39)}$$

Thus we see that the quantum mechanical features can be included with an essentially classical framework in terms of the effective potential.

APPENDIX G

INFORMATION THEORY

So far we have discussed the basic formulae on the basis of the Gibbs ensemble theory. An alternative approach to deal with the problem is based on information theory, which we consider in this Appendix.

In order to introduce the basic concept of measuring "information", we consider a simple problem of choosing between n possibilities, all of them are equally probable. Due to certain lack of information it is difficult to decide among the possibilities. The amount of uncertainly H is taken as some function H(n) of the n possibilities. The function H(n) has some specific properties:

(i) The function H(n) is a positive number

(ii) If $n \geq m$, $H(n) \geq H(m)$

(iii) $H(nm) = H(n) + H(m)$

(iv) If there is only one possibility, there is no uncertainty, i.e. $H(a) = 0$.

It was shown by Shannon in 1948 that the uncertainty function may be defined as

$$H(n) = K \ln n \tag{G.1}$$

where K is a positive constant. Eq.(G.1) is taken as a measure of the uncertainty before an event occurs.

Next we consider a choice among n possibilities. Let ρ_i be a probability assigned to each event such that

$$\rho_i \geq 0$$

$$\Sigma \rho_i = 1 \qquad (i = 1, 2, ..., n) \tag{G.2}$$

We consider all possible sequences of N events of which N_1 events are type1, N_2 events of type 2, and so on such that $N = \Sigma_i N_i$

$$\rho_i = N_i / N$$

The number of permutations of these N events is $N! / (\Pi N_i!)$. Since one does not know the order in which the events appear, the uncertainty associated with one group of N events of n assorted types is

$$H = K \ln [N! / (\Pi N_i)]$$

$$= K [N \ln N - N - \Sigma N_i \ln N_i - \Sigma N_i]$$

$$= K \Sigma N_i \ln (N / N_i)$$

$$= - K N \Sigma \rho_i \ln \rho_i \qquad (G.3)$$

So the average uncertainty per event is

$$H(n) = - K \sum_{i=1}^{n} \rho_i \ln \rho_i \qquad (G.4)$$

If the events are equally probable $\rho_i = 1/n$ and Eq.(G.1) changes into Eq.(G.1). This equation is known as the Shannon measure of information uncertainty.

In stead of using the uncertainty H, some time we prefer to use information I defined by

$$I = K \sum_{i} \rho_i \ln \rho_i = - H \qquad (G.5)$$

when the uncertainty H is maximum the information is minimum and vice versa. If we chose K = k, Eq.(G.5) gives the information, theoretic entropy. If the information is minimum, the corresponding uncertainty is maximum, and all the accessible microstate of the closed thermodynamic system is equally probable. This is the principle of equal a priori probability.

Putting $\rho_i = 1/ \Delta\Gamma$ in Eq.(G.5), we get

$$H = - K \Sigma (1 / \Delta\Gamma) \ln (1 / \Delta\Gamma) = K \Sigma (1 / \Delta\Gamma) \ln \Delta\Gamma \qquad (G.6)$$

Since there are total of $\Delta\Gamma$ terms in the summation, all of which are equal to $(1 / \Delta\Gamma) \ln \Delta\Gamma$, we have

$$H = k \ln \Delta\Gamma \qquad (G.7)$$

where $\Delta\Gamma$ is the statistical weight of a closed system. Comparing with Eq.(3.4.13), we can write the entropy in the form

$$S = H = -I \qquad (G.8)$$

Eq.(6.8) establishes the close connection between the uncertainty H and entropy S or the close connection between information 1 and entropy (–S).

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